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**DETERMINATION OF MERCURY
IN FISH TISSUE
PART I: PERFORMANCE CRITERIA**

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DETERMINATION OF MERCURY IN FISH TISSUE
PART I: PERFORMANCE CRITERIA

Based on 32 samples analyzed by 16 labs
in eight studies between July 1987 and June 1991.

Distributed by the Freshwater Institute
Department of Fisheries and Oceans.

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PART 1: PERFORMANCE CRITERIA

BASED ON 32 SAMPLES ANALYZED BY 16 LABS
IN EIGHT STUDIES BETWEEN JULY 1987 AND JUNE 1991
DISTRIBUTED BY THE FRESHWATER INSTITUTE
DEPARTMENT OF FISHERIES AND OCEANS

ABSTRACT

This report summarizes various aspects of laboratory performance based on data collected by the Freshwater Institute (FWI), Department of Fisheries and Oceans, Winnipeg. Laboratory performance criteria have been calculated for the analysis of Mercury in canned fish based on an evaluation of within and between laboratory estimates of standard deviation. The evaluation is based on a set of five laboratories, selected from among 16, who displayed the least bias and best precision over a series of 8 sets of 4 canned fish tissue samples distributed between July 1987 and June 1991. Samples fell in the concentration range of 0.1 to 1.6 ppm Hg.

The interlaboratory sample average value excluding outliers (FWI Avg), as reported by FWI for each sample, was used to assess group and individual laboratory performance. The within-laboratory standard deviation was approximately $S_w = 0.008 + 3.6\% \text{ FWI Avg} \pm 0.004 \text{ ppm Hg}$. The 'best 5' of 16 laboratories were very well controlled, with an interlaboratory long-term precision of approximately $S = 0.004 + 4.1\% \text{ FWI Avg} \pm 0.007 \text{ ppm Hg}$, very similar to the in-laboratory estimate. Their individual average bias was less than $\pm 0.02 \text{ ppm}$ with an average intersample standard deviation of 0.02 to 0.04 ppm Hg. An added five laboratories displayed occasional bias of 0.02 to 0.045 ppm and poorer interstudy precision. For these 'better 10' facilities the interlaboratory precision was $S = 0.011 + 5.9\% \text{ FWI Avg} \pm 0.017 \text{ ppm Hg}$. The remaining six laboratories displayed chronic control problems but demonstrated an underlying comparable ability. Individual laboratory control problems appear to stem from determinate, systematic, errors such as bias in stock standards, inadequate slope control, or error in baseline/blank settings from study to study. Based on this review, achievable performance criteria can be set for laboratories performing Mercury analysis on the canned fish tissue samples provided by FWI. Although the precision of preparation and homogeneity of the fish samples would be expected to contribute to overall error, its actual impact appears to be small compared to laboratory precision.

Keywords: mercury, fish, tissue, laboratory, performance

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INTRODUCTION

This review was initiated to determine whether performance criteria could be set for contract laboratory analysis of mercury in fish. The interpretation of long-term environmental trends and effects requires careful and continuing control of analytical bias. The most frequent sources of determinate error include accuracy of standards, inadequate calibration control, laboratory contamination, and inappropriate corrections for method blank or baseline effects. Ability to maintain long-term precision that is comparable to the single-analyst within-day repeatability of a test is the mark of a controlled laboratory. This ability is best evaluated by the analysis of a series of 'unknown' actual matrix samples of demonstrated homogeneity and stability.

In the early 1970's, the Inspection Services staff at the Freshwater Institute (FWI), Department of Fisheries and Oceans, Winnipeg initiated a series of 'round-robin' studies using samples of canned fish prepared for this purpose. These studies have continued on a more or less regular 4 month basis for the past two decades. For the past few years there have been 20 to 30 participants in each study. Each analyst is requested to provide triplicate measurements on two different days, for each of the 4 different samples. Samples are not repeated from one study to the next. Laboratories participate on a voluntary basis, and are not identified by name in the study reports.

The complete FWI data base covers twenty years, many samples, and a variety of laboratories. Even for the four years evaluated in this report, it provides a remarkable insight into long-term analytical control and the ability of individual laboratories to demonstrate control. FWI staff prepare a summary report which lists the average and standard deviation of the replicate results reported by each participant for each sample. They calculate an overall average and standard deviation for all participants. They also report a sample average (excluding outliers) and corresponding standard deviation for the data from those participants not identified as a statistical outlier. The FWI outlier procedure iteratively excludes data which differs by more than 2 standard deviations from the current overall average.

This review summarizes the performance of only those laboratories which provided results for each of 32 samples, submitted in 8 sets of 4 samples each, between July 1987 and June 1991, in order to examine the possibility for setting performance criteria based on the . The data from other laboratories which participated less frequently in these studies is not used.

EVALUATION AND OBSERVATIONS

Data was entered into a spreadsheet for each sample/participant based on the summary reports prepared by FWI staff. For most purposes the data was then evaluated relative to the average (excluding outliers) as reported by FWI in each study summary.

Differences from FWI Avg: Distribution Plots (Table 1, 1a, Figures 1, 2, and Appendix)

A table of residual differences (Table 1) was prepared as follows: the FWI interlaboratory sample average (previously calculated by FWI staff excluding outliers) was subtracted from each analyst's average result. The average residual difference was determined for each laboratory (across samples), and corresponding standard deviations were calculated. Table 1 is sorted horizontally based on the average difference reported by each laboratory.

Figure 1 indicates the level of bias associated with each laboratory, (sorted in order from negative to positive bias). It is clear that laboratories 01, 07, 16, 17, and 37 are least biased on average.

Table 1a was prepared by sorting these residual differences according to magnitude. Figure 2 shows the broad distribution of these differences. Although it appears to be more or less normally distributed, this distribution incorporates several distinct populations of laboratory performance. The Appendix includes diagrams showing the distribution for each laboratory. But it also includes line diagrams for each set of 4 samples to demonstrate that these residual differences frequently incorporate a significant level of either intercept or slope bias. (For further discussion refer to the Appendix.)

Individual Long-term Laboratory Precision (Table 1, Figures 3, 4)

Figure 3 shows for each laboratory the standard deviation of their residual differences. It is apparent that the six least biased laboratories demonstrate better long-term precision for these 8 studies. Laboratory 3's poorer precision prevented its inclusion among the best laboratories.

In the following review, laboratories 01, 07, 16, 17, and 37 are discussed as the 'best five' labs. These facilities plus laboratories 03, 05, 31, 43, and 57 are discussed as the 'better 10' labs. The remaining facilities 02, 11, 19, 31, 46, and 47 have sporadic or chronic problems. The individual performance diagrams suggest that most of these facilities do produce acceptable data fairly regularly.

Interlaboratory Sample Standard Deviations (Table 1, 2a, Figures 4, 5, 6)

The residual differences in Table 1 were also averaged for each sample (across laboratories), and summarized in table 2a. Figures 4, 5, and 6, show the relationship of S vs FWI Avg for all 16, the 'best 5' and the 'better 10' facilities respectively. Because sample #191 (1.61 ppm) was somewhat isolated from the rest of the sample concentrations (next highest value was 1.15 ppm), it was excluded in determining the regression equation.

Because all outliers were included in preparing figure 4, there is no clear relationship between S and FWI Avg. But based on the values tabulated by FWI for the S associated with their FWI Average (excluding outliers) sample concentration, the equation would be:

$$\begin{array}{ll} \text{FWI estimate:} & S = 0.017 + 5.6\% \text{ FWI Avg ppm Hg, } (r = 0.76) \quad (S_{y.x} = 0.014) \\ \text{where:} & \text{FWI Avg} = \text{interlab average concentration (excluding outliers)} \end{array}$$

Based on the data shown in figures 5 and 6, the equations for interlaboratory reproducibility are:

$$\begin{array}{ll} \text{the better 10 labs:} & S = 0.011 + 5.9\% \text{ FWI Avg ppm Hg, } (r = 0.73) \quad (S_{y.x} = 0.017) \\ \text{the best 5 labs:} & S = 0.004 + 4.1\% \text{ FWI Avg ppm Hg, } (r = 0.88) \quad (S_{y.x} = 0.007) \end{array}$$

For the 'best five' laboratories, the estimate includes labs (07, 17, 37) which showed somewhat less long-term precision than labs 01 and 16 (see appendix). Some of the data for the laboratories that are being reviewed in this report were obviously excluded from the FWI Avg as 'outliers'. And the FWI Avg includes data from laboratories which reported measurements for some but not all of the samples in the 8 studies being evaluated here, and which are therefore not included in this evaluation. The comparability of these equations confirms the general reliability of these estimates of interlaboratory precision for the purpose of setting performance criteria (see below).

Within-lab Standard Deviation (Sw) (Table 3, 2b, figures 7, 8, 9, 10)

Table 3 records the individual estimates of Sw derived from the replicate measurements reported by each analyst for each sample as summarized by FWI staff. The average Sw per lab is summarized in Table 2b and figure 7. This information provides an estimate of the best precision possible. As expected, it is reasonably constant (at about 0.02 ppm) for most laboratories. Even the 'less-controlled' laboratories demonstrate acceptable repeatability on a per sample basis (labs 55 and 05 show the poorest repeatability).

The dependence of Sw on sample concentration is shown in figures 8, 9, and 10. variability, is summarized below (based on the data in table 2b) for all 16 labs, the 'best 5', and the 'better 10' respectively. For the 'best 5' laboratories, the average interlaboratory Sw is barely dependent of the sample concentration. Because sample #191 (1.61 ppm) was somewhat isolated from the rest of the sample concentrations (next highest value was 1.15 ppm), it was excluded in determining the regression equation. Based on linear regression, the equation for interlaboratory repeatability varies only slightly, if at all, depending upon the particular labs included.

$$\begin{array}{ll} \text{for all 16 labs:} & Sw = 0.008 + 3.6\% \text{ FWI Avg } \pm 0.004 \text{ ppm Hg,} \\ \text{the better 10 labs:} & Sw = 0.011 + 2.7\% \text{ FWI Avg } \pm 0.005 \text{ ppm Hg,} \\ \text{the best 5 labs:} & Sw = 0.010 + 2.0\% \text{ FWI Avg } \pm 0.004 \text{ ppm Hg,} \\ \text{where:} & \text{FWI Avg} = \text{interlab average concentration (excluding outliers)} \end{array}$$

These equations apply in the range 0.09 to 1.2 ppm Hg. These estimates of Sw will be somewhat affected by the fact that the individual estimates of Sw per lab/sample were reported by FWI to only one significant figure.

Performance Criteria (Table 4, figures 11, 12)

Based on these observations, summary plots were prepared with the data from the 'best 5' facilities. Table 4 lists the median value reported per sample by the 'best 5' labs. It also tabulates the standard deviation of the data reported by these laboratories for each sample, and calculates the individual differences per sample for each laboratory relative to their median value.

Figure 11 plots the FWI values versus the median for the 'best 5' laboratories. Figure 12 shows the dependence of S for the 'best 5' versus concentration, scaled so that it can be overlaid as the 'upper control limit' on figure 13. The following observations are noteworthy:

- 1) The medians of the best 5 laboratories are in close agreement with the FWI Avg.
$$(\text{FWI Avg} - \text{Median}) = -0.001 + 2.5\% \text{ Median}$$

The correlation coefficient $R = 0.387$ for this residuals equation indicates that the residuals slope of 2.5% is significantly different from zero. At an alpha of 0.05 the critical value for R is 0.35 for 30 degrees of freedom, (i.e., for this data set, over the long-term, the FWI Avg is slightly biased relative to the Median).

- 2) The between-lab standard deviation for the 'best 5' labs versus the Median is:
$$S = 0.004 + 4.2\% \text{ Median}$$

The equation for these same labs versus the FWI Avg. was:

$$S = 0.004 + 4.1\% \text{ FWI Avg.} \pm 0.007$$

- 3) These findings suggest that a performance Warning Limit and Control Limit could be set at:
$$\begin{aligned} \text{WL} &= \text{Median} \pm (0.008 + 0.08 \text{ FWI Avg}). \\ \text{CL} &= \text{Median} \pm (0.012 + 0.13 \text{ FWI Avg}). \end{aligned}$$

Figure 13 shows the individual data points for the 'best five' labs plotted versus their median value, and Warning and Control Limit lines have been drawn approximating these equations. In estimating these performance criteria we include only the variability of the 'best 5' data about their own median. This reduces the impact of occasional 'outliers' in this selected data set, and ensures an internally consistent reference point for determining the dependence of 'difference' on concentration.

The individual performance plots in the appendix tend to substantiate some risk of bias in any given FWI Average. This occurs because 'outliers' are only detected if there is sufficient 'good' data. A bias can be induced by the inclusion of apparently acceptable data from laboratories with demonstrated poorer control. Since an average is easily affected by undetected outliers, the median is a preferred basis for determining a consensus value among laboratories, provided there is a reasonable degree of central tendency in the data. But FWI Avg could be substituted, with due precautions, in the above CL and WL equations without affecting conclusion significantly.

SUMMARY

The Mercury in Fish Interlaboratory Study database, developed from the individual reports of FWI, has provided an excellent long-term overview of performance and control status. It is clear that most laboratories are capable of controlled performance. Laboratory performance criteria have been calculated for the analysis of Mercury in canned fish tissue based on an evaluation of within and between laboratory estimates of standard deviation. This evaluation is based on a limited set of five laboratories, selected from among 16, who displayed the least bias and best precision over a series of 8 sets of 4 canned fish tissue samples distributed between July 1987 and June 1991. The individual diagrams in the appendix confirm the general achievability of the performance criteria based on the data from the 'best 5' laboratories. A separate paper will address the performance of all laboratories that have participated in approximately 50 such studies over the past 20 years. It is possible that the lack of a specific performance criteria may have had an adverse effect on some environmental databases at some times in the past.

Note that the FWI average corrected for outliers does not necessarily reflect accuracy. It is a consensus value which may be biased. But it is interesting that the distribution of differences is tightest for those who are close to this consensus value. These facilities are both precise and controlled, their individual working standards are in good agreement, and their sample preparation procedures apparently provide consistent recovery.

In controlled laboratories long-term precision is not particularly dependent on concentration. For the best laboratories it may be almost independent of concentration. The variability induced by sample preparation (concentration-independent) tends to dominate in controlled laboratories, whereas the variation in re-setting slope factors, or in preparing and using standards, (concentration-dependent) tends to dominate in less-well controlled laboratories. Several of the facilities that have contributed data to these FWI round-robins could benefit from an internal review of the accuracy of their stock standards; many could benefit from a more stringent control program for their standard response factor (slope); and some seem to have occasional problems with baseline/blank corrections. But this review also suggests that these analysts (and by inference the others whose data was not used in this evaluation) have the capability to perform equally well.

Based on the analysis of canned fish tissue as provided by FWI, these findings suggest that a performance Warning Limits (WL) and Control Limits (CL) could be set at:

$$WL = \text{Median} \pm (0.008 + 0.08 \text{ FWI Avg}).$$

$$CL = \text{Median} \pm (0.012 + 0.13 \text{ FWI Avg}).$$

Note that these criteria are based on the average of 6 replicate measurements (two separate sets of triplicates). They include allowance for interlaboratory and between-day variability. They should be considered for establishing in-laboratory control by those wishing to ensure that their data quality will meet a standard set by their peers.

The consistent reliability of the fish samples provided by FWI ensures a reliable, and reasonable, basis for decisions about control status. It may be possible to review (decrease) the number of

samples submitted per study and the number of replicates required per sample and yet retain the ability to flag potential analytical control problems. The average repeatability of the replicate measurements appears to be adequate compared to the variability induced by inadequate control.

FWI Summary Reports round-off the averages and standard deviations of the individual laboratory replicates to the nearest 0.01 ppm Hg. The presence of an additional significant figure would have improved the quality of the estimates of precision and bias attempted in this review. The effect of round-off is seen in the distribution of differences plots as a deficiency of odd-valued differences or gaps. The presence of an additional significant digit would have provided smoother distributions and better estimates of bias and variability. When applying the Warning and Control Limits suggested from this evaluation it would be advisable to record the average per sample to the nearest 0.001 ppm Hg.

If one wishes to monitor small trends in the mercury content of fish over extended periods of time it may be advisable to require replicate analysis of at least some fish samples, regular verification of working mercury standards and calibration factors, and careful evaluation of sources of baseline or blank related determinate error.

ACKNOWLEDGEMENTS

Marilyn Hendzel, Al Rieger and Erin Burns-Flett, Inspection Services, Department of Fisheries and Oceans, Central and Arctic Region, at FWI, have provided immeasurable service to the laboratory community by maintaining these studies over this extended period of time. They are to be commended for the quality of the samples distributed, since the performance of even the best laboratories is limited by the care with which such samples are prepared and split. There is no evidence that sample splitting has affected this interlaboratory performance evaluation.

FWI Study Reports used in this Evaluation

<u>SAMPLE SET</u>	<u>DATE SAMPLES SENT</u>	<u>DATE OF REPORT</u>
180-183	17 Jul., 1987	29 Oct., 1987
184-187	8 Jan., 1988	16 May, 1988
188-191	27 Jun., 1988	14 Oct., 1988
192-195	23 Dec., 1988	20 Apr., 1989
200-203	13 Oct., 1989	30 Jan., 1990
204-207	16 Apr., 1990	27 Jun., 1990
208-211	8 Aug., 1990	11 Dec., 1990
216-219	Jun., 1991	28 Aug., 1991

Note: sample analyses were to be performed on a specified date about 1 month after date submitted.

TABLES AND DIAGRAMS

TABLE 1: DIFFERENCES BETWEEN LAB RESULTS AND THE FWI AVERAGE

TABLE 1a: DISTRIBUTION OF DIFFERENCES FROM TABLE 1 PER LAB
Plus Summary of Distribution: Best 5, Better 10, Overall

TABLE 2a: SUMMARY PER SAMPLE FROM TABLE 1 (Avg.Diff & Std.Dev of Diff)
+ Summary of Interlab Std.Dev: (Best 5, Better 10, All 16 labs)

TABLE 2b: SUMMARY PER SAMPLE FROM TABLE 2 (Avg. Sw & Std.Dev of Sw)
Plus Summary of In-Lab Std.Dev: Best 5, Better 10, Overall

TABLE 3: IN-LAB Sw ESTIMATES (AS REPORTED IN FWI STUDY SUMMARIES)

TABLE 4: PERFORMANCE CHARACTERISTICS (DATA FROM BEST 5 LABS)

TABLE 5: INDIVIDUAL PERFORMANCE VS CONTROL AND WARNING LIMITS

FIGURE 1: AVERAGE DIFFERENCE FROM FWI Avg (32 samples per lab)

FIGURE 2: DISTRIBUTION OF DIFFERENCES ABOUT FWI Avg (all 16 labs, 32 samples)

FIGURE 3: STANDARD DEVIATION OF DIFFERENCES (32 samples per lab)

FIGURE 4: INTERLAB SD vs FWI Avg (All 16 labs, per sample)

FIGURE 5: INTERLAB SD vs FWI Avg (Best 5 labs, per sample)

FIGURE 6: INTERLAB SD vs FWI Avg (Better 10 labs, per sample)

FIGURE 7: AVERAGE IN-LAB STD DEV (Sw) (Summarized by FWI for each sample/lab)

FIGURE 8: WITHIN-LAB Sw vs FWI Avg (All 16 labs, per sample)

FIGURE 9: WITHIN-LAB Sw vs FWI Avg (Best 5 labs, per sample)

FIGURE 10: WITHIN-LAB Sw vs FWI Avg (All 16 labs, per sample)

FIGURE 11: COMPARISON OF FWI AVERAGE vs MEDIAN (Best 5 labs)

FIGURE 12: INTERLAB STD DEV vs MEDIAN (Best 5 labs)

FIGURE 13: WARNING AND CONTROL LIMITS FOR DIFFERENCE FROM MEDIAN
Plotted values are the Best 5 labs' differences from medians

TABLE 1: DIFFERENCES BETWEEN LAB RESULTS AND THE FWI AVERAGE (Corrected for outliers)

Sorted by average difference per lab (Across) and sample # (Down)

TABLE 1a: DISTRIBUTION OF DIFFERENCES (TABLE 1) PER LAB

DIFFERENCE IN CYCLO DISTRIBUTION																
Diff. (ppm)	# of labs included															
	5	10	16													
-0.20
-0.17
-0.16
-0.15
-0.14
-0.13
-0.12
-0.11
-0.10
-0.09
-0.08
-0.07
-0.06
-0.05
-0.04
-0.03
-0.02
-0.01
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.10
0.11
0.12
0.13
0.14
0.15
0.16
0.17
0.18
0.19
0.20
0.21
0.22
0.23
0.24
0.27
0.28
0.32
0.33
0.34
0.35
0.39

Summary of Overall Distribution

Diff. (ppm)	# of Labs Included
-0.20	3
-0.17	2
-0.16	1
-0.15	3
-0.14	1
-0.13	1
-0.12	4
-0.11	2
-0.10	1
-0.09	1
-0.08	3
-0.07	3
-0.06	4
-0.05	8
-0.04	7
-0.03	11
-0.02	15
-0.01	25
0.00	11
0.01	17
0.02	34
0.03	20
0.04	1
0.05	39
0.06	50
0.07	24
0.08	9
0.09	11
0.10	3
0.11	7
0.12	51
0.13	14
0.14	22
0.15	31
0.16	22
0.17	11
0.18	8
0.19	15
0.20	9
0.21	6
0.22	6
0.23	3
0.24	5
0.27	1
0.28	2
0.32	4
0.33	8
0.34	7
0.35	4
0.39	6

Fig. 1: AVERAGE DIFFERENCE PER LAB

Averaged for 32 Samples/Lab

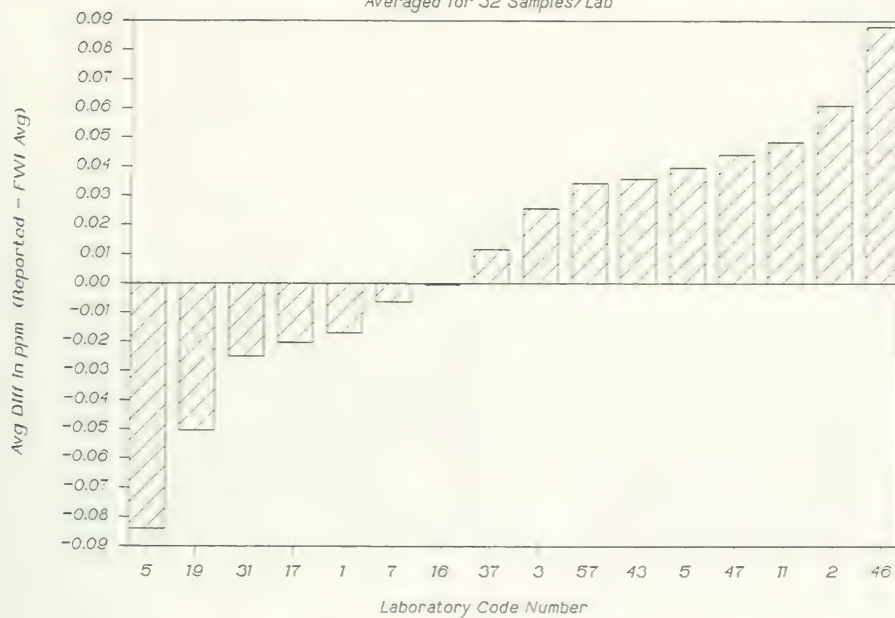


Fig. 2: DIFFERENCES FROM FWI AVG.

Distribution for 16 Labs, 32 Samples

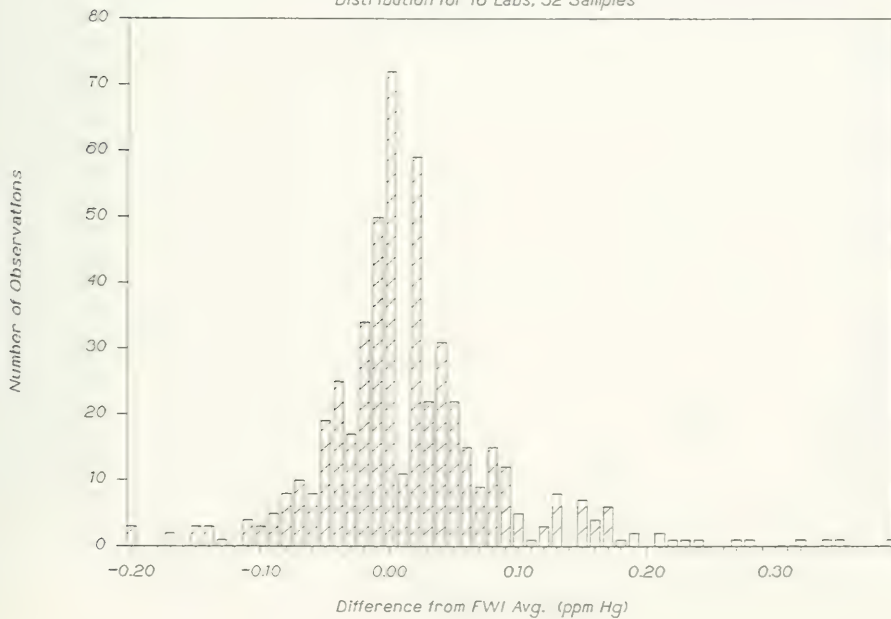


Fig. 3: STD DEV OF DIFFERENCES PER LAB

Based on 32 Samples/Lab

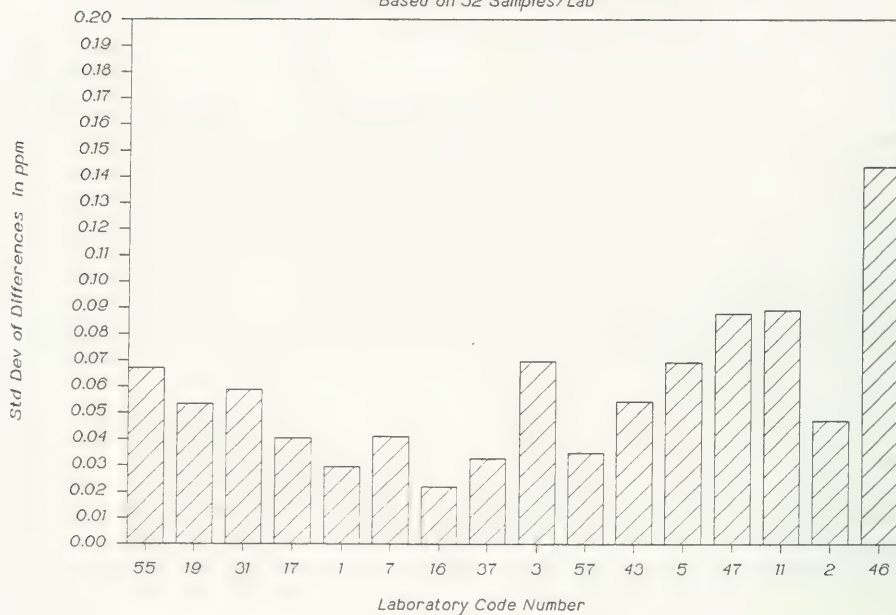


Fig. 4: INTERLAB STD DEV PER SAMPLE

for All 16 Labs

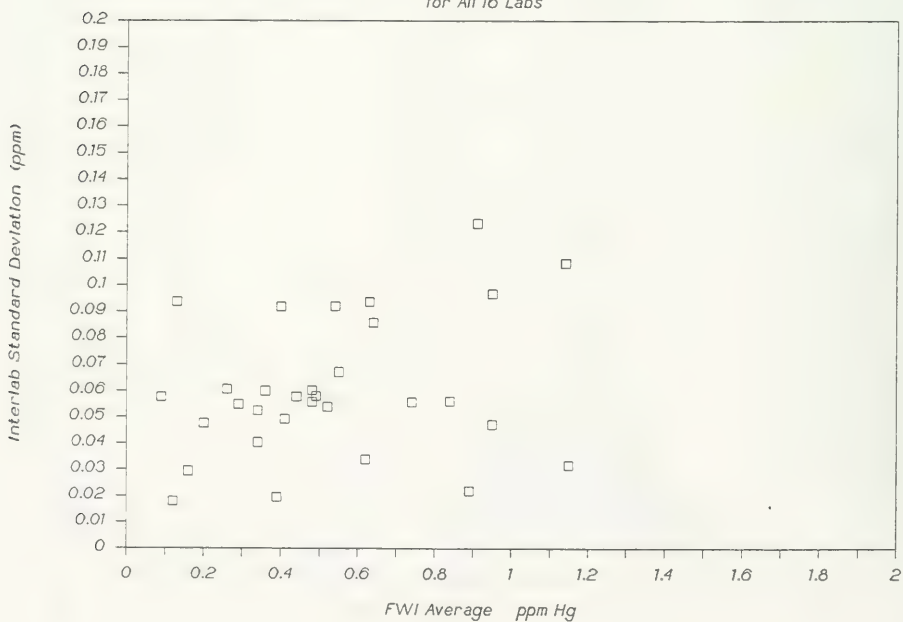


Fig. 5: INTERLAB STD DEV PER SAMPLE
for Best 5 Labs

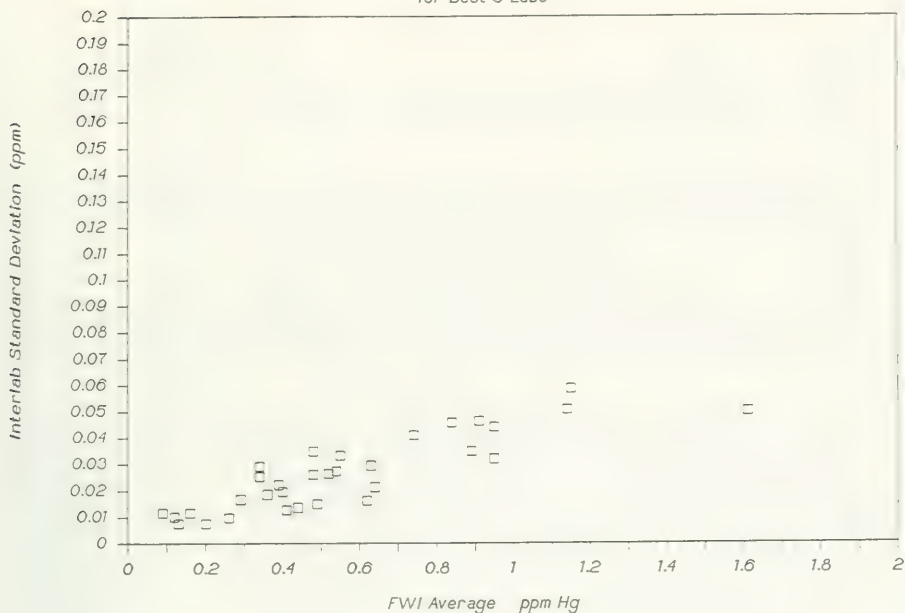


Fig. 6: INTERLAB STD DEV PER SAMPLE
for Better 10 Labs

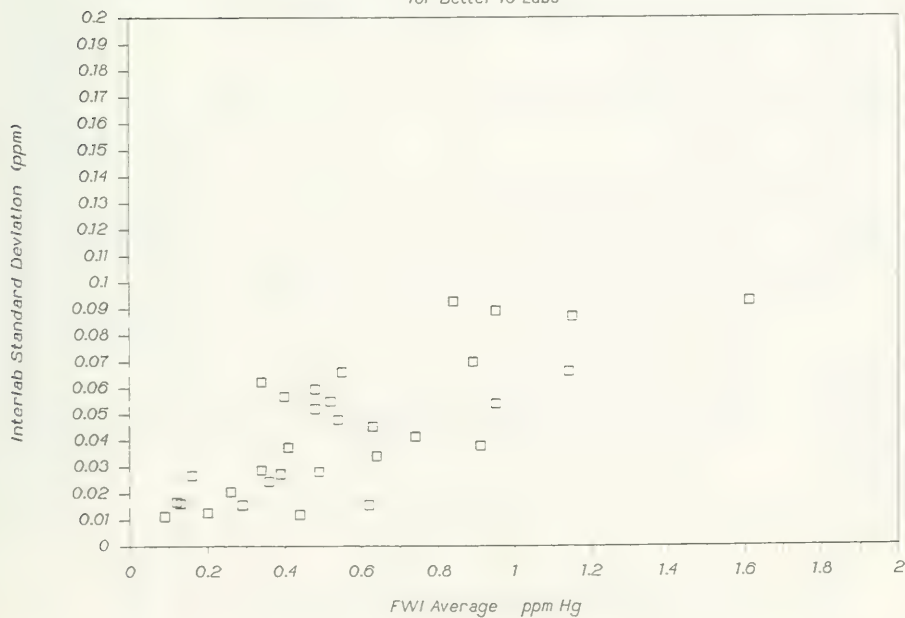


TABLE 2a: SUMMARY PER SAMPLE FROM TABLE 1
(Avg.Diff & Std.Dev of Diff)

Sample	FWI DATA SUMMARY BETWEEN-LAB		DIFFERENCES SUMMARY	
	Avg.	Std.Dev.	BETTER 10 Avg. Std.Dev.	BEST 5 Avg. Std.Dev.
180	0.16	0.03	21 0.012 0.027	0.002 0.012
181	0.48	0.05	20 0.017 0.060	-0.030 0.026
182	0.52	0.05	20 0.020 0.055	-0.012 0.026
183	0.95	0.08	19 0.031 0.089	-0.034 0.044
184	0.12	0.02	24 -0.005 0.017	-0.014 0.010
185	0.48	0.04	23 0.018 0.052	-0.018 0.035
186	0.74	0.03	21 -0.012 0.041	-0.040 0.041
187	1.14	0.05	19 0.002 0.066	-0.014 0.051
188	0.20	0.03	20 0.006 0.013	0.002 0.007
189	0.36	0.05	20 0.006 0.025	0.006 0.019
190	0.64	0.05	18 0.015 0.034	0.018 0.021
191	1.61	0.14	18 0.075 0.093	0.064 0.050
192	0.84	0.08	22 0.026 0.093	0.008 0.046
193	0.34	0.04	23 0.005 0.062	-0.010 0.025
194	0.55	0.06	23 0.016 0.066	-0.004 0.033
195	0.40	0.03	19 0.021 0.057	0.006 0.020
200	0.39	0.03	19 -0.011 0.027	-0.022 0.022
201	0.95	0.05	18 0.012 0.054	-0.024 0.032
202	0.49	0.03	20 0.008 0.028	-0.016 0.015
203	0.13	0.02	21 -0.005 0.016	-0.012 0.007
204	0.89	0.08	20 -0.011 0.070	-0.034 0.035
205	0.34	0.04	22 -0.005 0.029	-0.012 0.029
206	0.09	0.01	21 0.001 0.011	-0.002 0.012
207	0.54	0.08	25 0.010 0.048	0.006 0.027
208	1.15	0.09	21 -0.003 0.087	-0.010 0.059
209	0.41	0.04	18 -0.007 0.037	-0.010 0.013
210	0.26	0.03	19 -0.009 0.021	-0.012 0.010
211	0.63	0.07	22 -0.013 0.045	0.004 0.029
216	0.62	0.04	21 -0.004 0.016	-0.014 0.016
217	0.29	0.04	25 -0.006 0.016	-0.010 0.017
218	0.44	0.03	21 0.004 0.012	0.004 0.014
219	0.91	0.09	24 0.036 0.038	0.026 0.046

Regression Output: (sample #191 excluded):

Between-lab Standard Deviation Data vs. FWI Avg.	
Best 5	10 labs FWI est.
0.004	0.011 0.017
Constant (Intercept)	0.041 0.059 0.056
X Coefficient (Slope)	0.004 0.010 0.009
Std Err of Coeff.	0.007 0.017 0.014
Std Err of Y Estimate	0.884 0.729 0.762
Correl'n Coeff. (R)	31 31
No. of Observations	31

TABLE 2b: SUMMARY PER SAMPLE FROM TABLE 2
(Avg. Sw & Std.Dev of Sw)

Sample	AVERAGE SW		STD.DEV SW	
	ALL BETTER 10	BEST 5	ALL BETTER 10	BEST 5
180	0.015 0.013 0.014	0.007 0.006 0.005	0.016 0.010 0.009	0.16 0.07 0.06
181	0.022 0.015 0.012	0.019 0.010 0.007	0.48 0.019 0.010	0.48 0.019 0.007
182	0.024 0.022 0.020	0.011 0.009 0.006	0.52 0.011 0.009	0.52 0.011 0.006
183	0.043 0.034 0.034	0.027 0.007 0.008	0.95 0.027 0.007	0.95 0.027 0.007
184	0.012 0.011 0.010	0.005 0.003 0.000	0.12 0.005 0.003	0.12 0.005 0.003
185	0.033 0.028 0.018	0.025 0.020 0.012	0.48 0.025 0.020	0.48 0.025 0.020
186	0.029 0.023 0.020	0.020 0.010 0.009	0.74 0.020 0.010	0.74 0.020 0.010
187	0.046 0.044 0.032	0.026 0.025 0.020	1.14 0.026 0.025	1.14 0.026 0.025
188	0.015 0.013 0.012	0.008 0.005 0.004	0.20 0.008 0.005	0.20 0.008 0.005
189	0.019 0.018 0.014	0.013 0.012 0.005	0.36 0.013 0.012	0.36 0.013 0.012
190	0.025 0.023 0.018	0.013 0.013 0.004	0.64 0.013 0.013	0.64 0.013 0.013
191	0.024 0.072 0.052	0.082 0.059 0.019	1.61 0.082 0.059	1.61 0.082 0.059
192	0.044 0.046 0.024	0.044 0.052 0.005	0.84 0.044 0.052	0.84 0.044 0.052
193	0.026 0.027 0.016	0.023 0.026 0.005	0.34 0.023 0.026	0.34 0.023 0.026
194	0.031 0.035 0.022	0.029 0.033 0.007	0.55 0.031 0.033	0.55 0.031 0.033
195	0.029 0.031 0.018	0.033 0.040 0.010	0.40 0.033 0.040	0.40 0.033 0.040
200	0.023 0.023 0.020	0.009 0.009 0.011	0.39 0.009 0.009	0.39 0.009 0.009
201	0.023 0.040 0.028	0.026 0.021 0.012	0.95 0.026 0.021	0.95 0.026 0.021
202	0.024 0.024 0.020	0.011 0.009 0.006	0.43 0.011 0.009	0.43 0.011 0.009
203	0.011 0.011 0.010	0.006 0.007 0.006	0.13 0.006 0.007	0.13 0.006 0.007
204	0.042 0.036 0.022	0.035 0.021 0.007	0.89 0.042 0.036	0.89 0.042 0.036
205	0.017 0.015 0.016	0.008 0.007 0.008	0.34 0.017 0.015	0.34 0.017 0.015
206	0.014 0.018 0.010	0.021 0.026 0.011	0.09 0.014 0.018	0.09 0.014 0.018
207	0.028 0.029 0.030	0.013 0.013 0.009	0.54 0.028 0.029	0.54 0.028 0.029
208	0.054 0.038 0.030	0.049 0.027 0.014	1.15 0.054 0.038	1.15 0.054 0.038
209	0.029 0.027 0.026	0.018 0.017 0.014	0.41 0.029 0.027	0.41 0.029 0.027
210	0.018 0.018 0.012	0.015 0.016 0.004	0.26 0.018 0.018	0.26 0.018 0.018
211	0.031 0.025 0.024	0.022 0.007 0.005	0.63 0.031 0.025	0.63 0.031 0.025
216	0.024 0.020 0.020	0.013 0.006 0.006	0.62 0.024 0.020	0.62 0.024 0.020
217	0.016 0.016 0.016	0.007 0.007 0.005	0.29 0.016 0.016	0.29 0.016 0.016
218	0.023 0.022 0.026	0.013 0.009 0.008	0.44 0.023 0.022	0.44 0.023 0.022
219	0.042 0.032 0.030	0.027 0.012 0.011	0.91 0.042 0.032	0.91 0.042 0.032

Average Within-lab Standard Deviation vs. FWI Avg.	
Best 5	Better 10 Overall
0.010	0.011 0.008
Constant (Intercept)	0.020 0.027 0.036
X Coefficient (Slope)	0.002 0.003 0.002
Std Err of Coeff.	0.004 0.005 0.004
Std Err of Y Est.	0.836 0.831
Correl'n Coeff. (R)	31 31
No. of Observations	31

TABLE 3: IN-LAB S_w ESTIMATES (AS REPORTED IN FWI STUDY SUMMARIES)

(Each lab analyzed each sample in triplicate)

[labs listed in order of average difference from FWI Average]

Sample	Lab# 55	19	31	17	1	7	16	37	3	57	43	5	47	11	2	46
180	0.02	0.02	0.01	0.01	0.02	0.01	0.02	0.01	0.02	0.02	0.00	0.00	0.01	0.01	0.03	0.02
181	0.06	0.07	0.03	0.01	0.02	0.02	0.00	0.01	0.02	0.00	0.03	0.01	0.02	0.01	0.01	0.03
182	0.02	0.05	0.04	0.02	0.03	0.02	0.01	0.02	0.01	0.02	0.02	0.03	0.02	0.01	0.03	0.03
183	0.07	0.13	0.03	0.03	0.04	0.02	0.04	0.04	0.03	0.04	0.03	0.04	0.02	0.01	0.06	0.05
184	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.03
185	0.05	0.09	0.01	0.02	0.01	0.01	0.04	0.01	0.02	0.07	0.05	0.04	0.01	0.01	0.02	0.07
186	0.08	0.07	0.02	0.03	0.03	0.01	0.02	0.01	0.03	0.03	0.01	0.04	0.02	0.01	0.02	0.03
187	0.10	0.07	0.08	0.01	0.05	0.03	0.06	0.01	0.07	0.04	0.02	0.07	0.04	0.02	0.02	0.04
188	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.02	0.02	0.01	0.04
189	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.02	0.01	0.05	0.02	0.01	0.02	0.05
190	0.04	0.01	0.01	0.02	0.02	0.02	0.02	0.01	0.03	0.01	0.04	0.05	0.03	0.02	0.02	0.05
191	0.34	0.04	0.05	0.04	0.09	0.05	0.04	0.04	0.07	0.03	0.24	0.07	0.15	0.06	0.07	0.12
192	0.07	0.03	0.02	0.02	0.02	0.03	0.03	0.02	0.04	0.04	0.04	0.20	0.02	0.01	0.04	0.07
193	0.04	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.04	0.02	0.02	0.10	0.01	0.01	0.02	0.05
194	0.03	0.01	0.03	0.03	0.01	0.02	0.03	0.02	0.04	0.03	0.01	0.13	0.01	0.01	0.02	0.01
195	0.04	0.01	0.02	0.03	0.01	0.01	0.03	0.01	0.02	0.01	0.02	0.15	0.01	0.02	0.02	0.05
200	0.03	0.03	0.02	0.04	0.01	0.02	0.02	0.01	0.03	0.02	0.03	0.03	0.01	0.01	0.03	0.03
201	0.10	0.06	0.06	0.02	0.03	0.04	0.04	0.01	0.03	0.04	0.04	0.09	0.01	0.01	0.05	0.06
202	0.05	0.03	0.02	0.02	0.02	0.03	0.02	0.01	0.02	0.02	0.04	0.04	0.01	0.02	0.02	0.02
203	0.01	0.01	0.02	0.01	0.01	0.01	0.02	0.00	0.00	0.01	0.02	0.01	0.01	0.01	0.01	0.01
204	0.16	0.03	0.01	0.02	0.03	0.03	0.02	0.01	0.06	0.05	0.06	0.07	0.02	0.02	0.04	0.04
205	0.03	0.02	0.01	0.01	0.01	0.03	0.02	0.01	0.02	0.01	0.01	0.02	0.01	0.01	0.02	0.03
206	0.01	0.00	0.01	0.00	0.01	0.01	0.03	0.00	0.09	0.00	0.01	0.02	0.00	0.01	0.01	0.01
207	0.05	0.03	0.01	0.04	0.02	0.03	0.04	0.02	0.05	0.04	0.01	0.03	0.01	0.01	0.03	0.03
208	0.22	0.05	0.02	0.04	0.02	0.05	0.03	0.01	0.02	0.02	0.07	0.10	0.02	0.08	0.05	0.06
209	0.07	0.02	0.01	0.04	0.03	0.03	0.02	0.01	0.02	0.02	0.02	0.07	0.01	0.02	0.04	0.03
210	0.04	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.06	0	0.02	0.03	0.01	0.03	0.01	0.01
211	0.11	0.03	0.02	0.02	0.03	0.02	0.03	0.02	0.02	0.03	0.02	0.04	0.01	0.05	0.03	0.02
216	0.05	0.06	0.01	0.02	0.02	0.02	0.01	0.03	0.02	0.02	0.03	0.02	0.02	0.02	0.02	0.01
217	0.02	0.03	0.01	0.02	0.02	0.01	0.01	0.02	0.02	0.01	0.01	0.03	0.01	0.01	0.01	0.01
218	0.06	0.02	0.02	0.02	0.03	0.02	0.02	0.04	0.01	0.02	0.01	0.02	0.01	0.03	0.02	0.01
219	0.13	0.05	0.01	0.03	0.05	0.03	0.02	0.02	0.03	0.04	0.04	0.05	0.04	0.01	0.06	0.06

Lab =

55 19 31 17 01 07 16 37 03 57 47 11 02 46

S_w Avg =

0.067 0.035 0.021 0.022 0.023 0.022 0.023 0.016 0.031 0.023 0.033 0.052 0.020 0.019 0.027 0.038

S_w S.D. =

0.068 0.028 0.016 0.011 0.016 0.011 0.012 0.010 0.020 0.016 0.041 0.044 0.025 0.016 0.016 0.023

Fig. 7: AVERAGE IN-LAB STD DEV (FWI)

2 sets of 3 Replicates, 32 samples

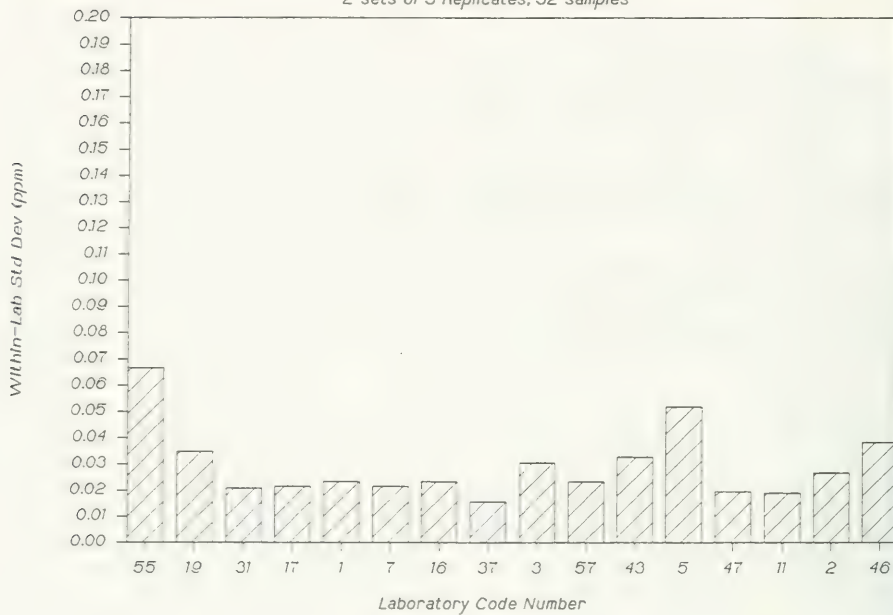
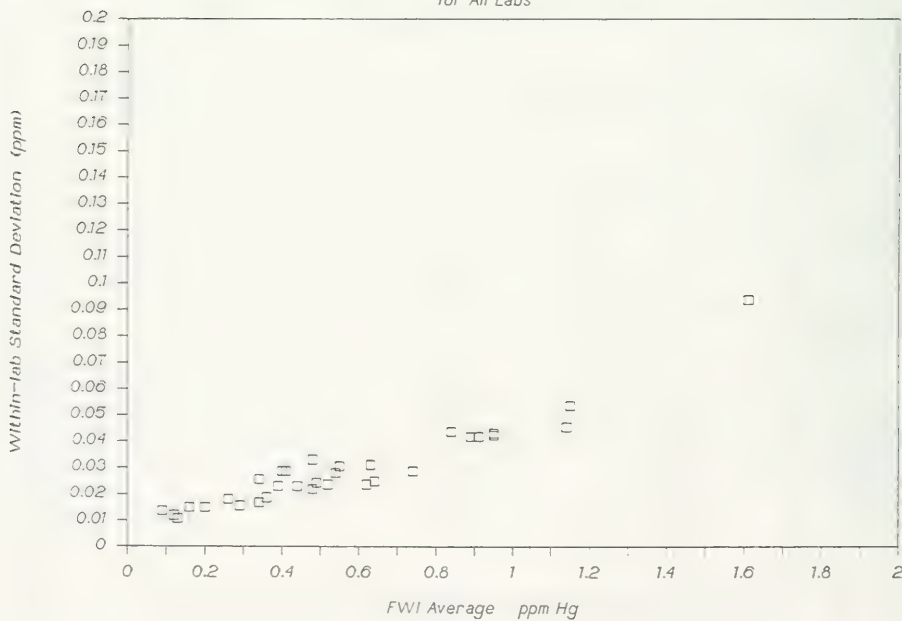
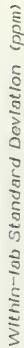


Fig. 8: WITHINLAB STD DEV vs FWI AVG

for All Labs



for 5 Best Labs



for 10 Better Labs

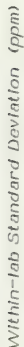


TABLE 4: PERFORMANCE CHARACTERISTICS BASED ON DATA FROM BEST FIVE LABS

SAMPLE NUMBER	AVG. FWL	BEST LABS		BEST LABS DIFFERENCES FROM THEIR MEDIAN				
		MEDIAN	SD.	Tab 01	07	16	17	37
180	0.16	0.160	0.01	-0.01	0.02	0.00	-0.01	0.01
181	0.48	0.460	0.03	0.01	0.01	-0.01	-0.06	0.00
182	0.52	0.520	0.03	-0.02	0.00	0.01	-0.06	0.01
183	0.95	0.940	0.04	-0.02	0.00	0.00	-0.11	0.01
184	0.12	0.110	0.01	-0.01	0.00	0.01	-0.02	0.00
185	0.48	0.460	0.03	0.00	0.04	0.03	-0.06	0.00
186	0.74	0.700	0.04	0.00	0.05	0.03	-0.07	-0.01
187	1.14	0.090	0.05	0.00	0.12	0.00	-0.01	0.07
188	0.20	0.200	0.01	0.00	0.01	0.00	-0.01	0.01
189	0.36	0.370	0.02	-0.02	0.00	0.02	-0.03	0.01
190	0.64	0.650	0.02	0.00	0.05	0.00	-0.01	0.00
191	1.61	1.670	0.05	0.00	0.09	-0.05	-0.04	0.02
192	0.84	0.850	0.05	-0.04	0.00	0.02	-0.06	0.07
193	0.34	0.340	0.03	-0.04	-0.05	0.03	0.00	0.00
194	0.55	0.540	0.03	-0.01	0.00	0.02	-0.04	0.06
195	0.40	0.400	0.02	0.00	0.00	0.01	-0.02	0.04
200	0.39	0.360	0.02	-0.01	-0.01	0.01	0.05	0.00
201	0.95	0.930	0.03	-0.01	-0.05	-0.01	0.00	0.05
202	0.49	0.470	0.01	-0.01	-0.01	0.01	0.03	0.00
203	0.13	0.120	0.01	0.00	-0.01	0.00	0.01	-0.01
204	0.89	0.830	0.03	0.00	-0.01	0.03	0.02	0.09
205	0.34	0.320	0.03	-0.01	0.00	0.04	-0.02	0.04
206	0.09	0.090	0.01	-0.02	-0.01	0.01	0.01	0.00
207	0.54	0.550	0.03	-0.03	-0.04	0.02	0.00	0.03
208	1.15	1.100	0.06	-0.01	0.00	-0.01	0.09	0.13
209	0.41	0.390	0.01	0.00	0.00	0.02	0.00	0.03
210	0.26	0.250	0.01	-0.02	0.00	0.01	0.00	0.00
211	0.63	0.630	0.03	0.00	-0.02	-0.02	0.00	0.06
216	0.62	0.610	0.02	-0.01	-0.03	0.02	0.00	0.00
217	0.29	0.280	0.02	-0.03	0.00	0.02	0.01	0.00
218	0.44	0.440	0.01	0.01	-0.02	0.02	0.01	0.00
219	0.91	0.920	0.05	0.08	-0.02	0.00	0.06	-0.04

FWL Avg.
vs Median
-0.001

Std. Dev.
vs Median
0.004

Regression Output for best five labs:

Constant (Intercept)
X Coefficient (Slope)
Std Err of Coefficient
Std Err of Y Estimate
Correlation Coeff (R)
No. of Observations

31

31

Fig. 11: FWI AVG VS MEDIAN BEST 5 LABS

Differences Plot

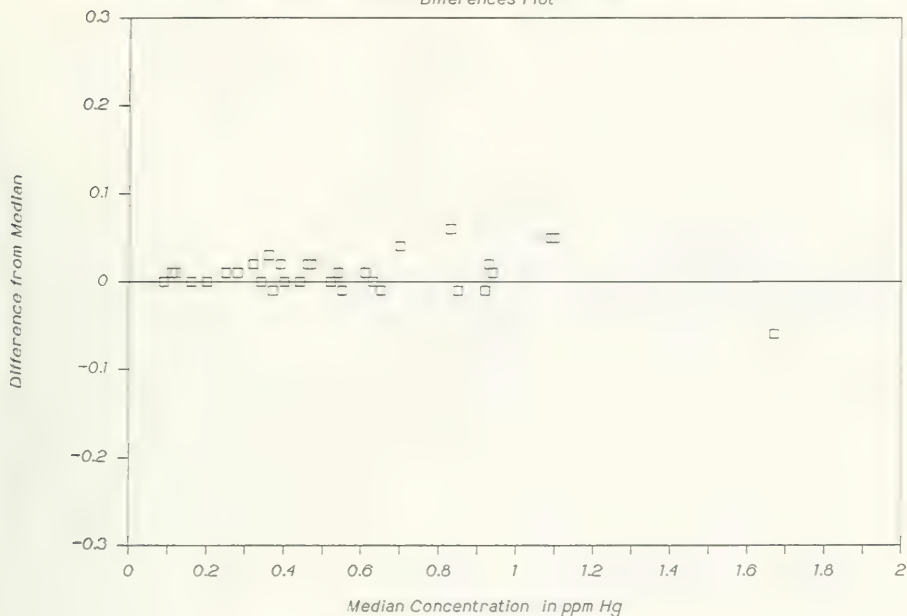


Fig. 12: INTERLAB STD DEV vs MEDIAN

For Data from Best 5 Labs

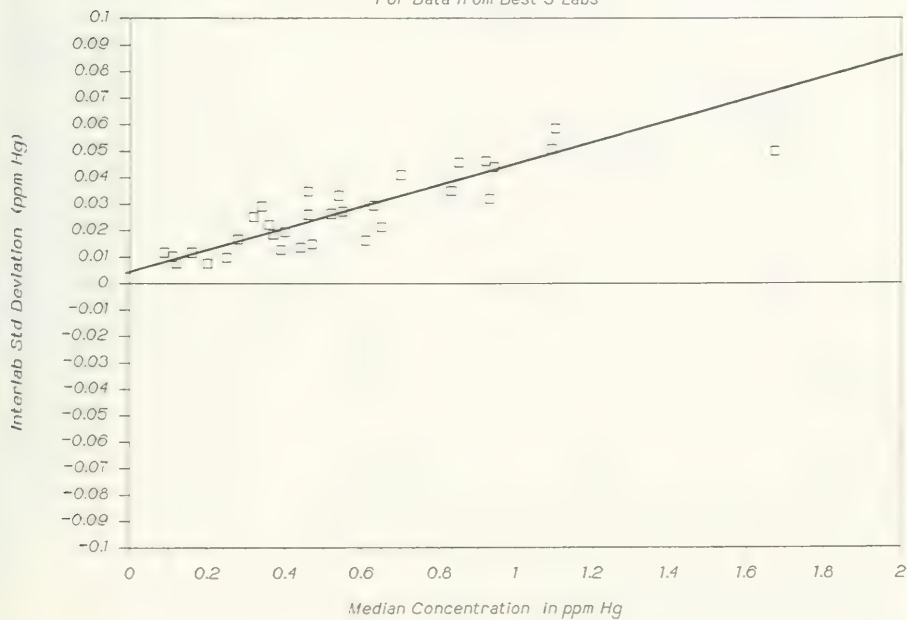


Fig. 13: WARNING AND CONTROL LIMITS

Differences from Medians (Best Labs)

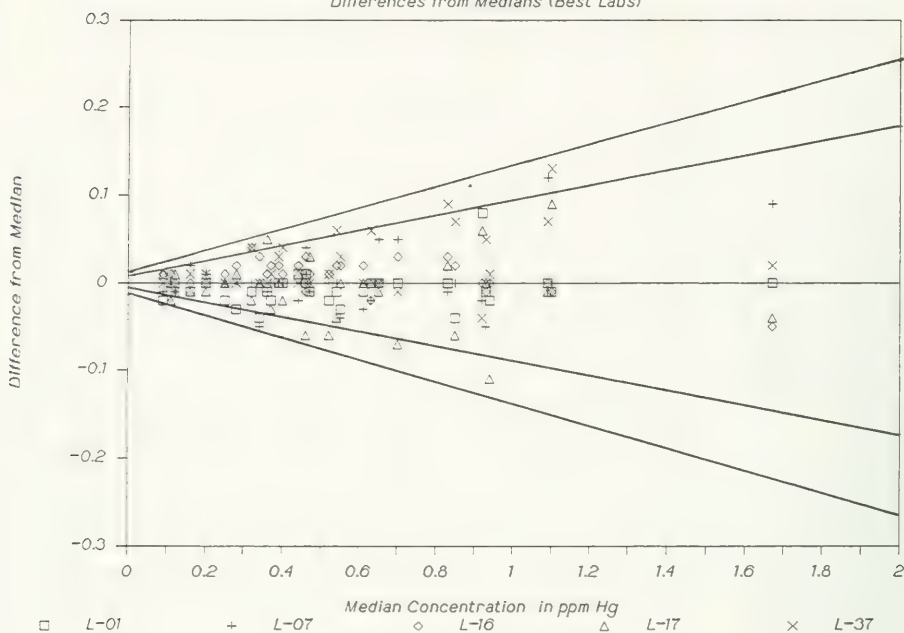


TABLE 5: EVALUATION OF PERFORMANCE VS CONTROL AND WARNING LIMITS

LOW or HIGH = outside control limits set at FWI Avg \pm (0.008 + 0.08 FWI Avg).
low or high = outside warning limits set at FWI Avg \pm (0.012 + 0.13 FWI Avg).

Sam#	Avg.	55	19	31	17	01	07	16	37	03	57	43	05	47	11	02	46
180	0.16	LOW	LOW	low						HIGH	HIGH		high				LOW
181	0.48	LOW			LOW					HIGH	high	high		low			HIGH
182	0.52				low					HIGH	high			low			high
183	0.95	LOW	LOW	high	low												HIGH
184	0.12	low	LOW	low	LOW	low				HIGH							HIGH
185	0.48	LOW		low	LOW					HIGH	HIGH	high					HIGH
186	0.74		low		LOW												HIGH
187	1.14			low										HIGH	high		HIGH
188	0.20	LOW									HIGH			HIGH	HIGH		HIGH
189	0.36	LOW	low	low								high		HIGH	HIGH		HIGH
190	0.64	LOW										high		HIGH	HIGH		HIGH
191	1.61	low					high		high				HIGH	HIGH	HIGH		HIGH
192	0.84	LOW															HIGH
193	0.34	LOW		LOW	LOW							high		HIGH	HIGH		HIGH
194	0.55	LOW		low	LOW								HIGH	HIGH	HIGH		HIGH
195	0.40	LOW											HIGH				HIGH
200	0.39	LOW												HIGH			LOW
201	0.95	LOW		high												high	
202	0.49	LOW										high		low			
203	0.13	LOW		high			low		low	LOW		high				HIGH	high
204	0.89	LOW	LOW	low	LOW	low	LOW		HIGH	high						HIGH	high
205	0.34		LOW	low		low	LOW			high						high	high
206	0.09					low				high						high	HIGH
207	0.54		LOW							HIGH			low	high		HIGH	HIGH
208	1.15			LOW							high						
209	0.41	LOW	LOW	LOW	LOW												low
210	0.26			LOW		LOW										HIGH	
211	0.63	LOW	LOW	LOW												HIGH	
216	0.62	LOW	LOW														high
217	0.29	LOW	LOW			LOW										high	HIGH
218	0.44	LOW	LOW	LOW		LOW								HIGH		high	HIGH
219	0.91					high								HIGH		HIGH	HIGH

APPENDIX:

INDIVIDUAL LABORATORY PERFORMANCE DIAGRAMS

Individual Laboratory Performance (Table 1a)

Table 1a was prepared to examine the distribution of differences for various laboratories and combinations of labs. Distribution plots were prepared for each laboratory. For some laboratories the differences from the sample average (excluding outliers as calculated by FWI staff) are quite tightly clustered, and some are more or less centred about a zero difference from this FWI Average value. In order to achieve this pattern, (for example lab #16) the analyst must have a good within-lab single-analyst repeatability, and must have maintained good control over sources of between-run biases including blank/baseline and calibration/slope corrections over the time frame of these eight studies (a period of four years).

Because the sample concentrations range from 0.1 to 1.6 ppm Hg, the data in table 1 was also used to examine any dependence of difference on sample concentration. These appear as the bottom diagram in each of the individual laboratory performance figures. Because each study involves four samples, the respective points were joined in order of increasing concentration for each study. In this type of residuals diagram, each set of four points should fit a reasonably straight line; fluctuation reflects repeatability or individual sample measurement problems. The intercept should be zero difference, and the slope should be zero; otherwise one suspects determinate error in calibration.

Note that the distribution diagram often presents an impression of normality. Therefore data points which differ because of a blank or slope related bias (as shown in the lower diagram of difference versus concentration) would generally not be detected as an outlier based on the usual tests for outliers. Data that is out-of-control cannot be used to determine effective control limits.

Individual Performance Evaluation

Table 5 shows the outcome of testing each laboratory result for difference from the FWI Avg. relative to the Warning or Control Limits specified above. Results beyond the control limits are identified as 'HIGH' or 'LOW'. Values beyond the Warning Limits are indicated 'high' or 'low'. The individual performance diagrams in the appendix also help to indicate the nature of any control problems. The following examples will assist the reader in investigating causes for the observed performance of individual laboratories.

Labs 01, 07, 16, 17, and 37 set the standard for long-term performance. Lab 01 has two atypical results. Lab 07 has 3 atypical results. Lab 17 is biased low in sets #108-187.

Lab 02 has had a continuing slope bias. The stock standard may be too strong.

Lab 03 had severe positive slope bias in set #180-184 and set #204-207.

Lab 05 had one severe blank/baseline problem for samples #192-195. The remaining data is reasonable. There is room for improved slope control.

Lab 11 has sporadic control problems including both intercept and slope biases. Sample sets #188-199 and #204-209 are particularly notable.

Lab 19 was biased low in sets #204-219. Slope control could be improved.

Lab 31 slope control could be improved.

Lab 43 data is well controlled but biased high on average, stock standard may be too weak?

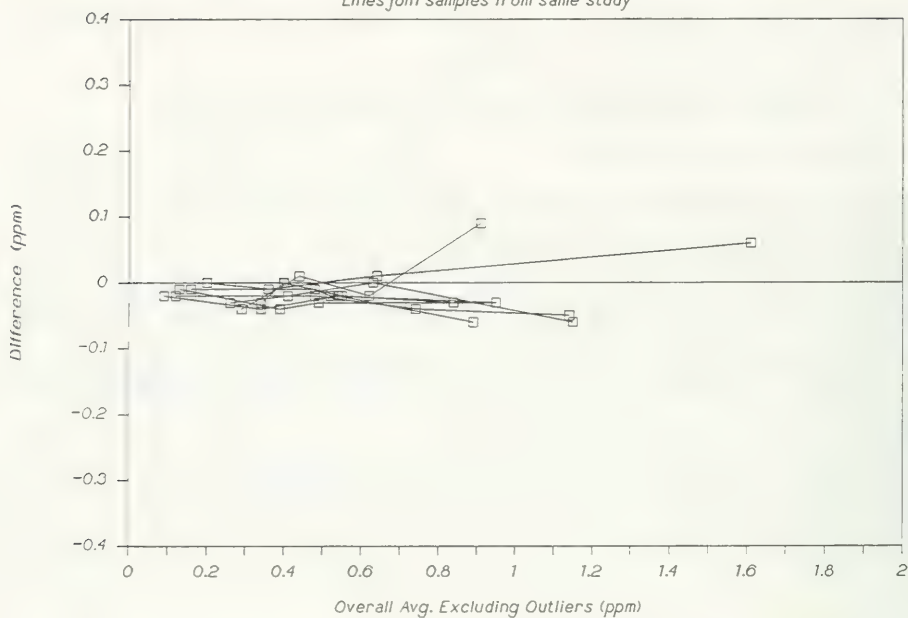
Lab 46 has a severe slope and intercept control problem.

Lab 47 had a slope problem for set #188-191, and some erratic values. Rest of data is well controlled.

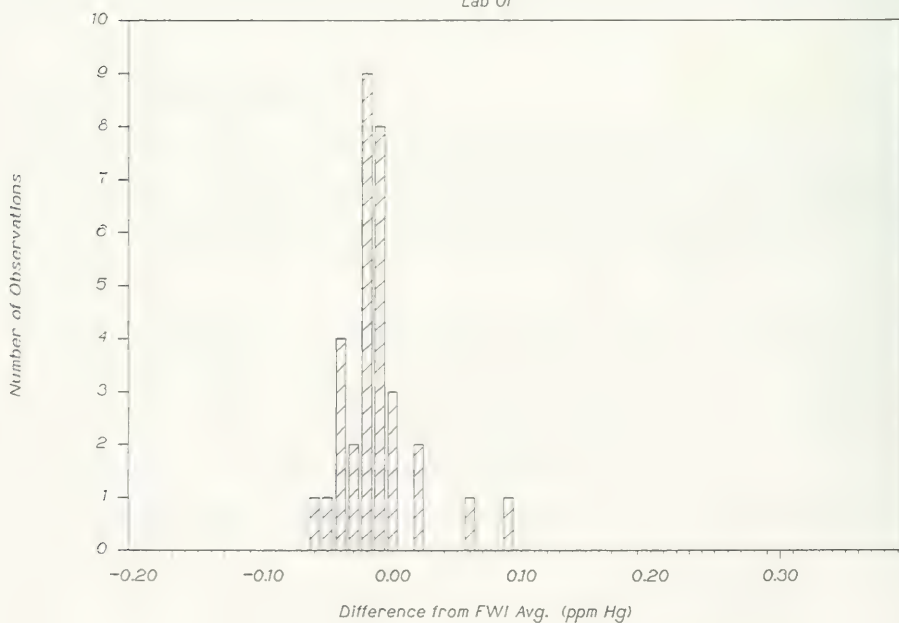
Lab 55 stock standard may be too strong. Bias obscured by significant variability in slope control. There may be a variable but generally low intercept problem (over-correction or inadequate control of baseline/blank?).

Lab 57 had (blank?) problems in samples #180-188. Otherwise control is good.

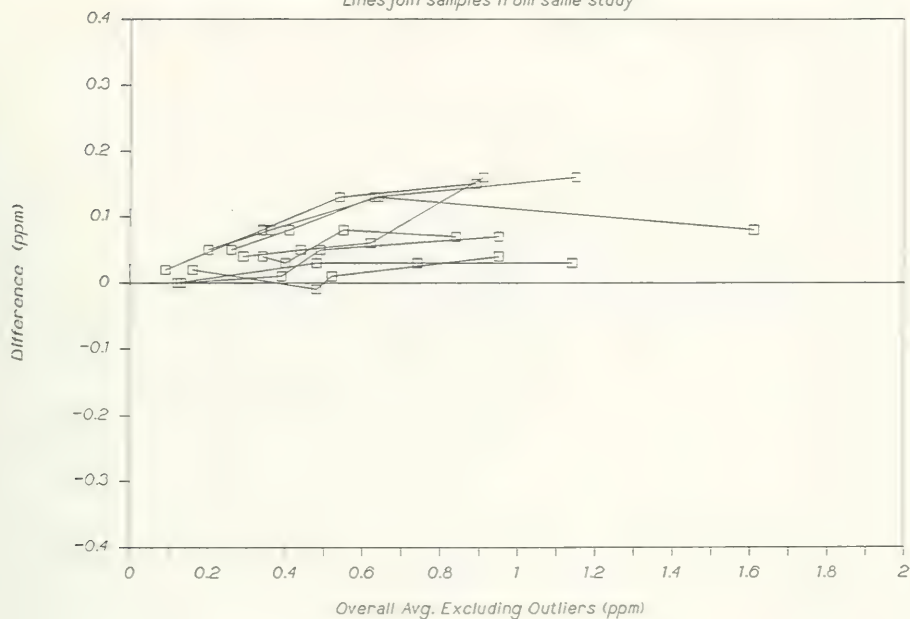
Lines join samples from same study



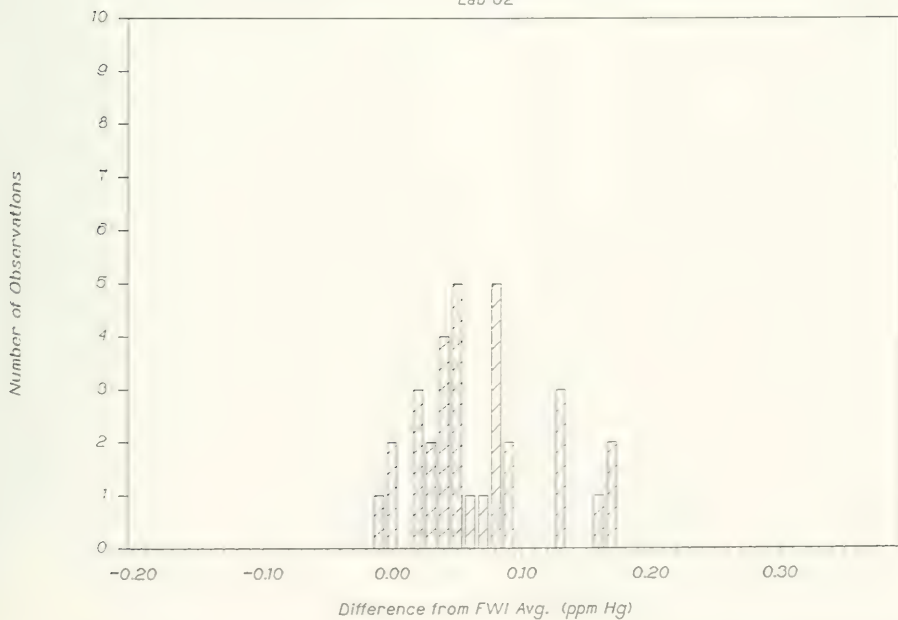
Lab 01



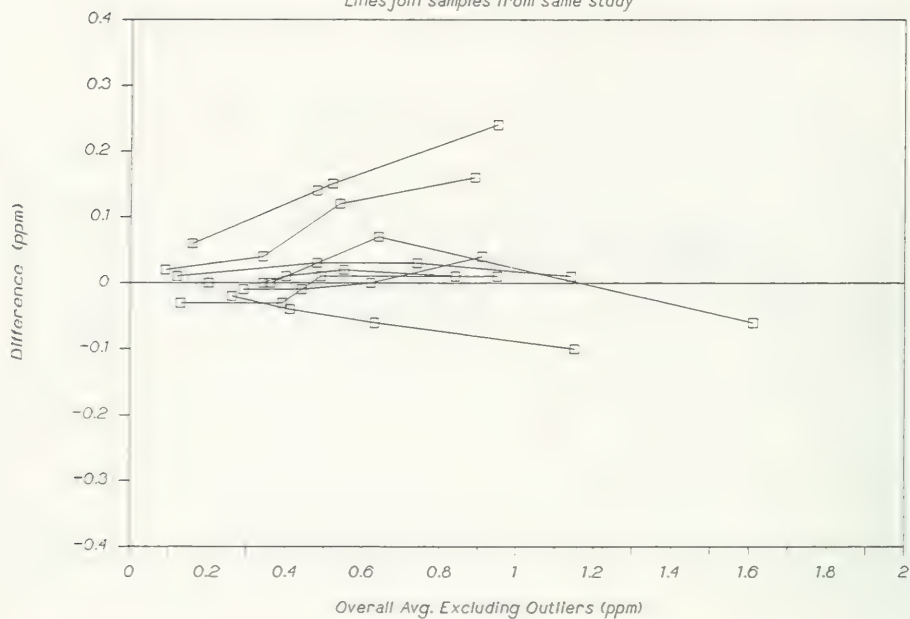
Lines join samples from same study



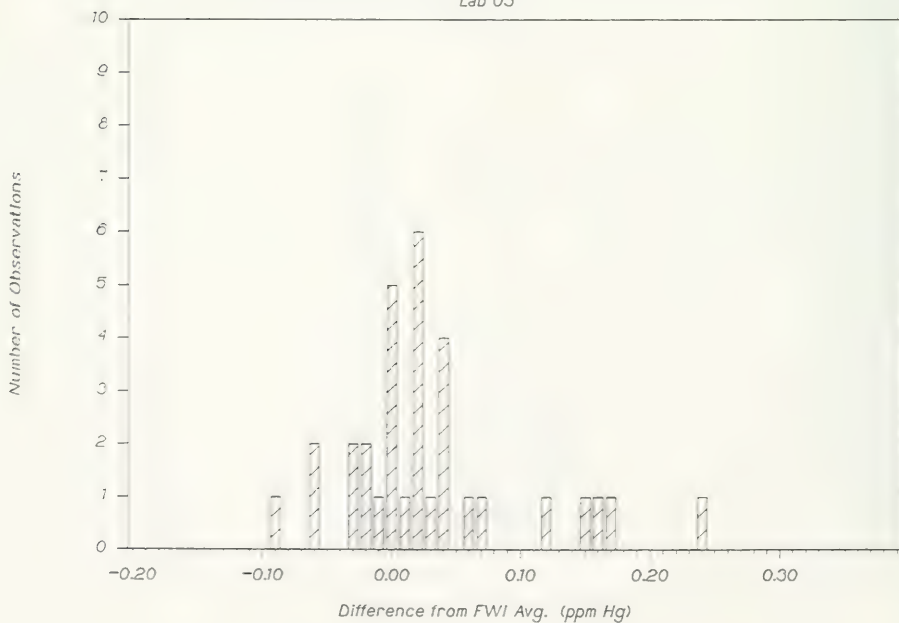
Lab 02



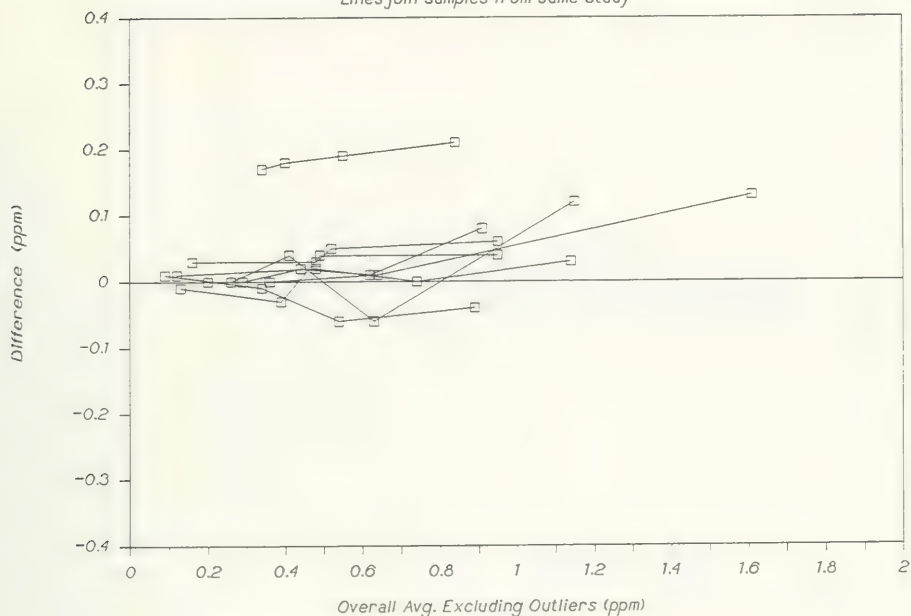
Lines join samples from same study



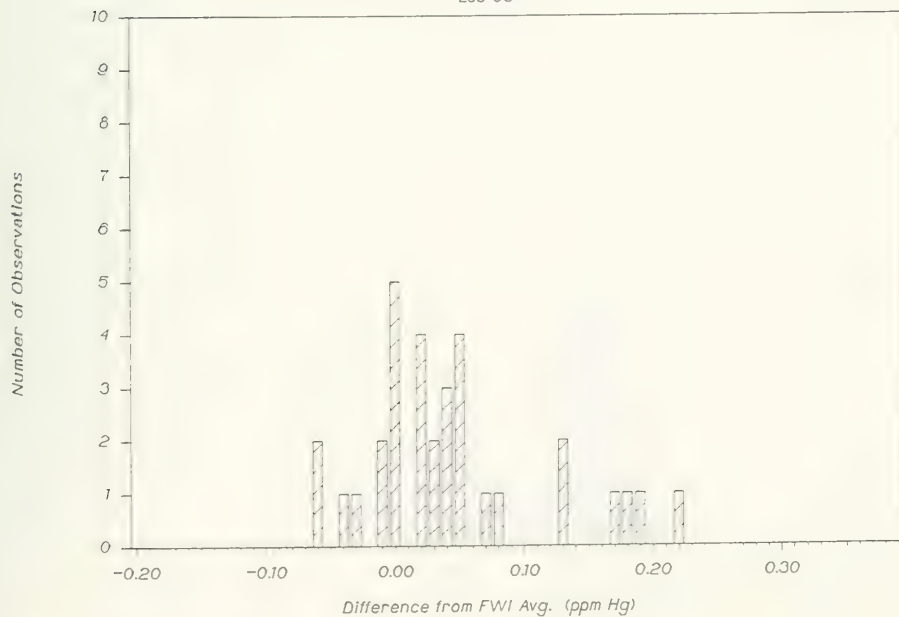
Lab 03



Lines join samples from same study

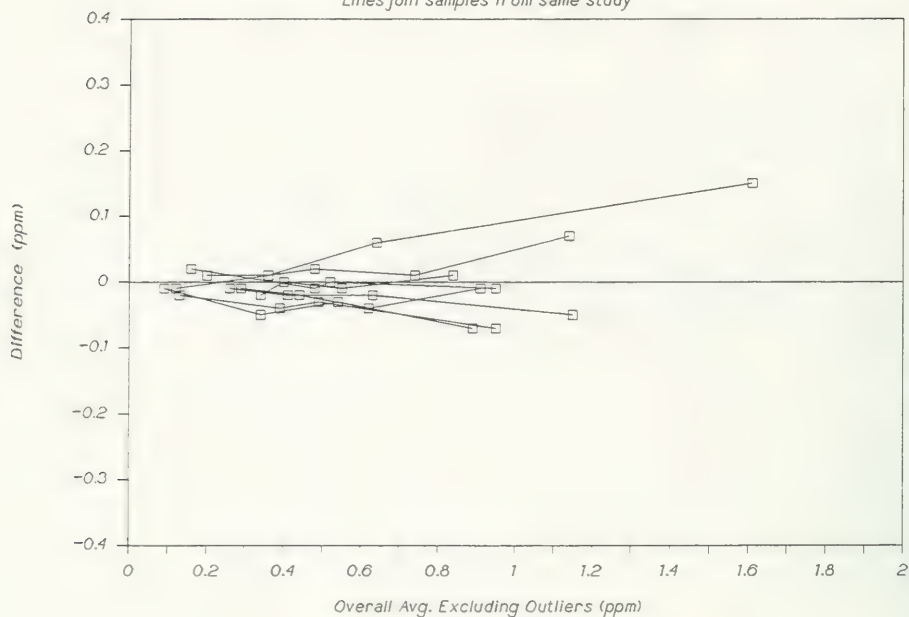


Lab 05



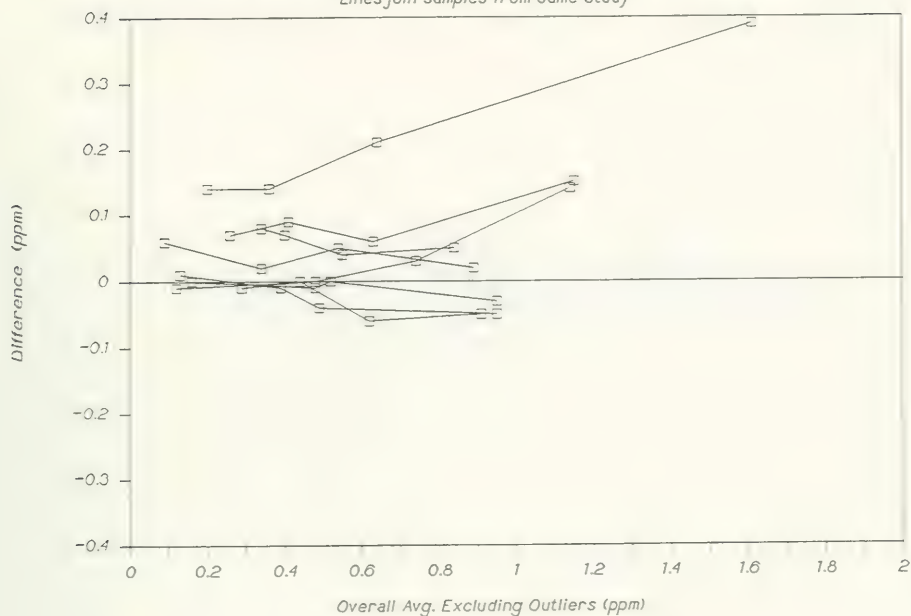
HG IN FISH: LAB 07 DIFFERENCES

Lines join samples from same study



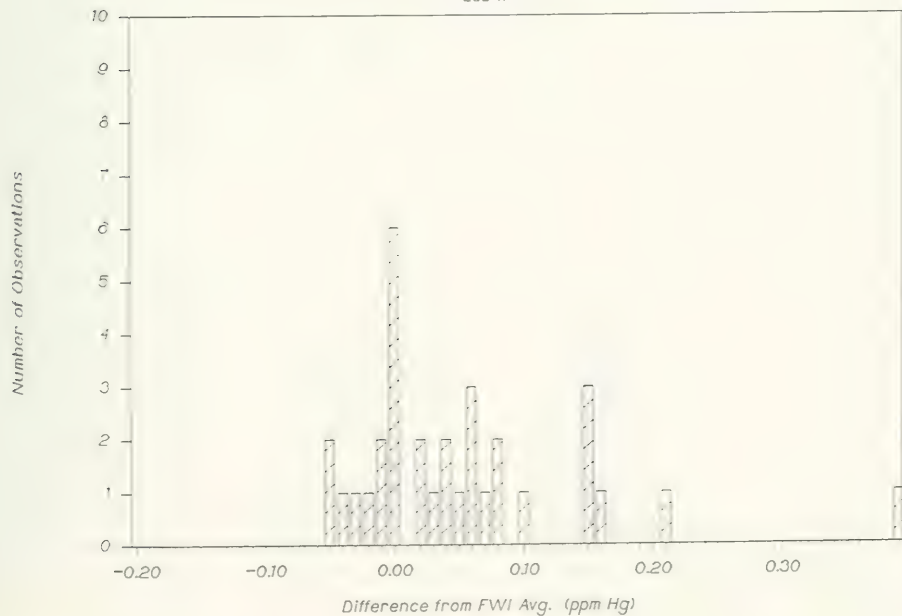
HG IN FISH: LAB 11 DIFFERENCES

Lines join samples from same study

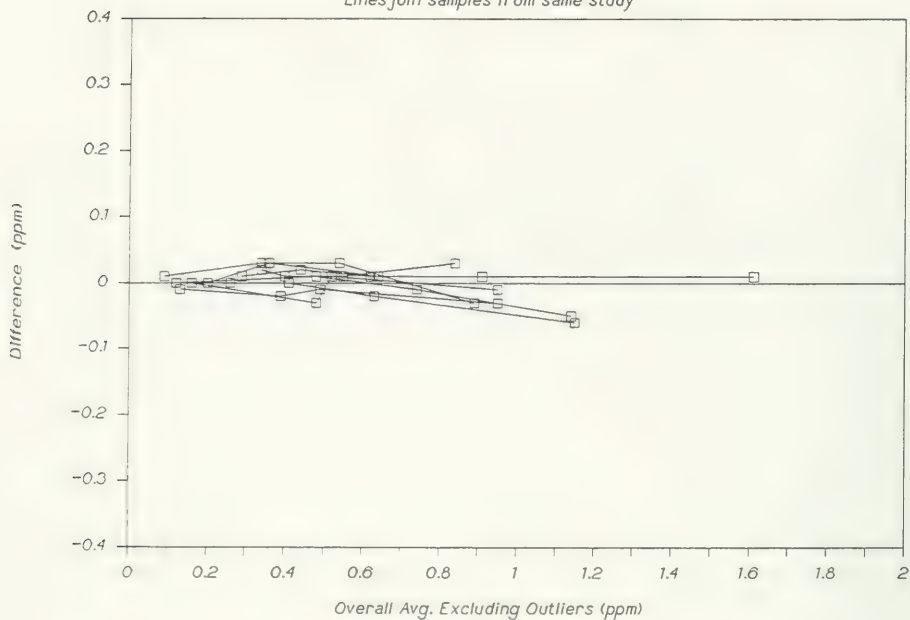


DIFFERENCES FROM FWI AVG.

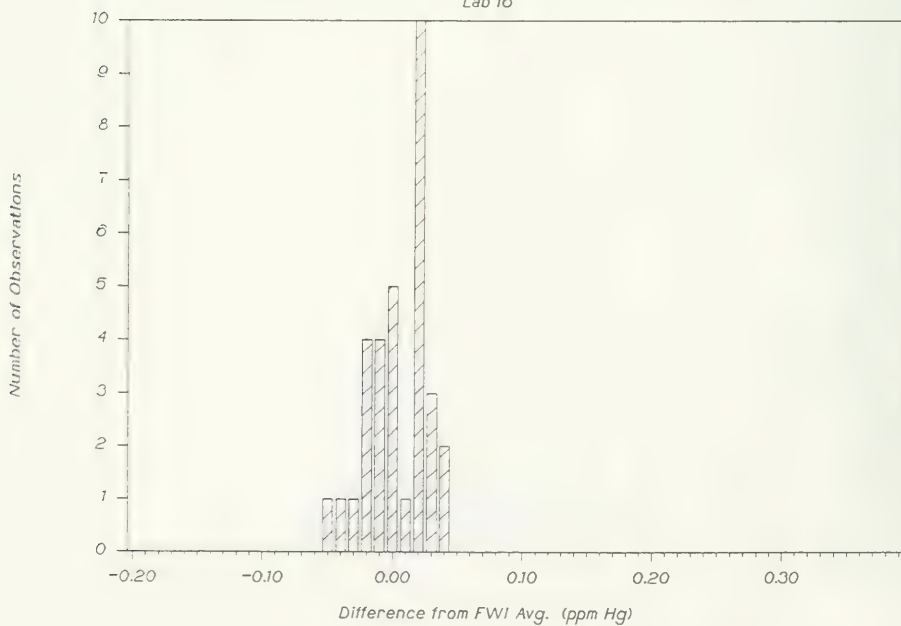
Lab 11



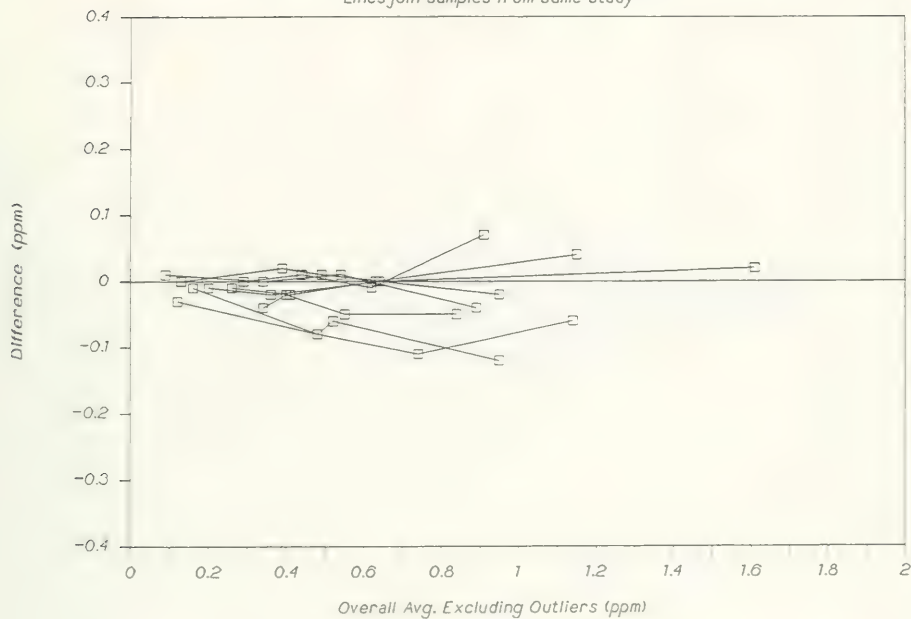
Lines join samples from same study



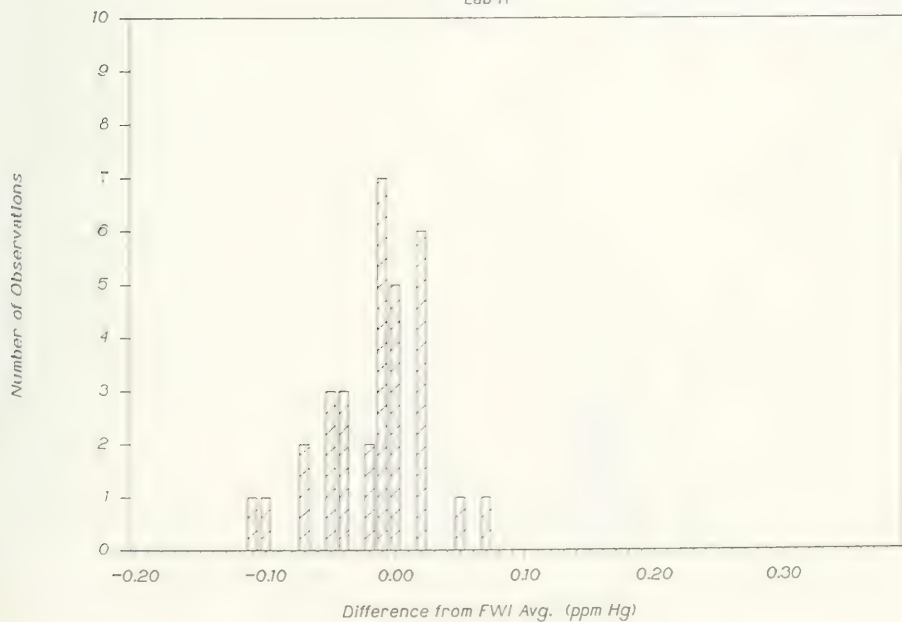
Lab 16



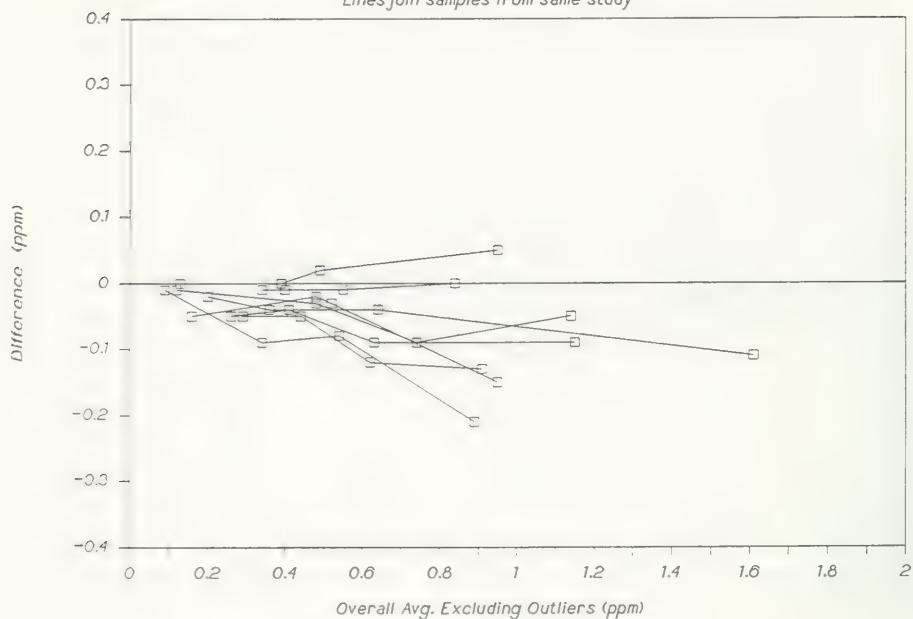
Lines join samples from same study



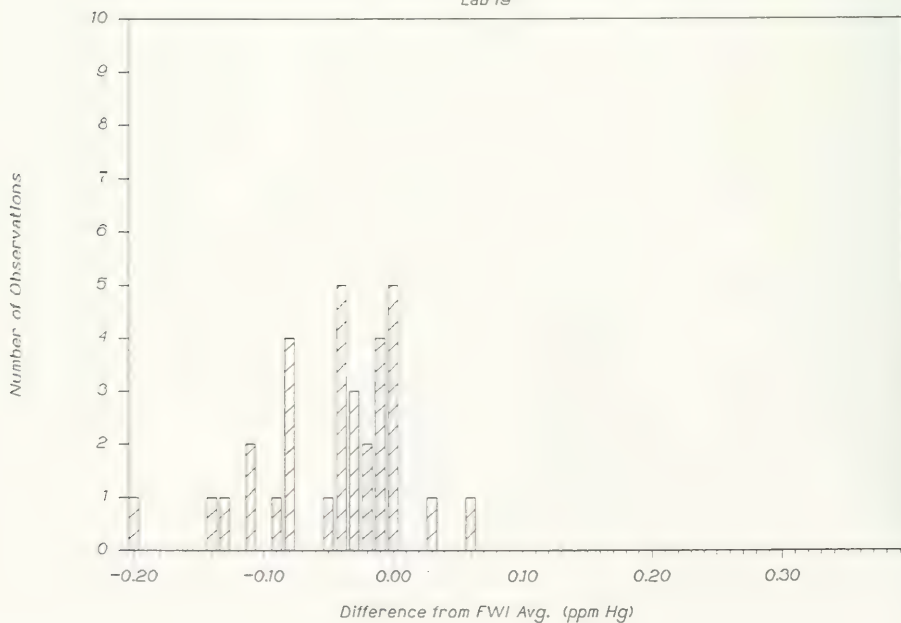
Lab 17



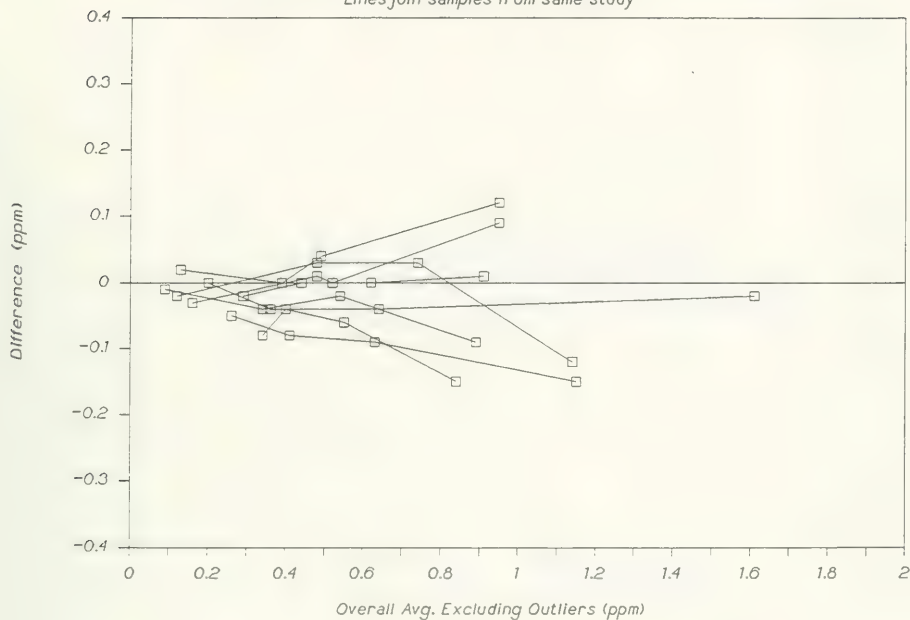
Lines join samples from same study



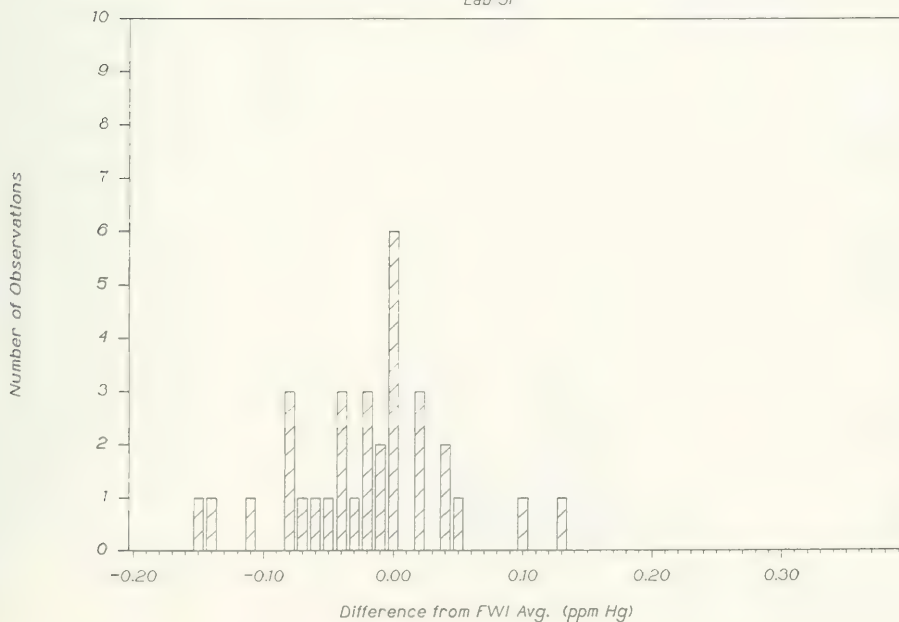
Lab 19



Lines join samples from same study

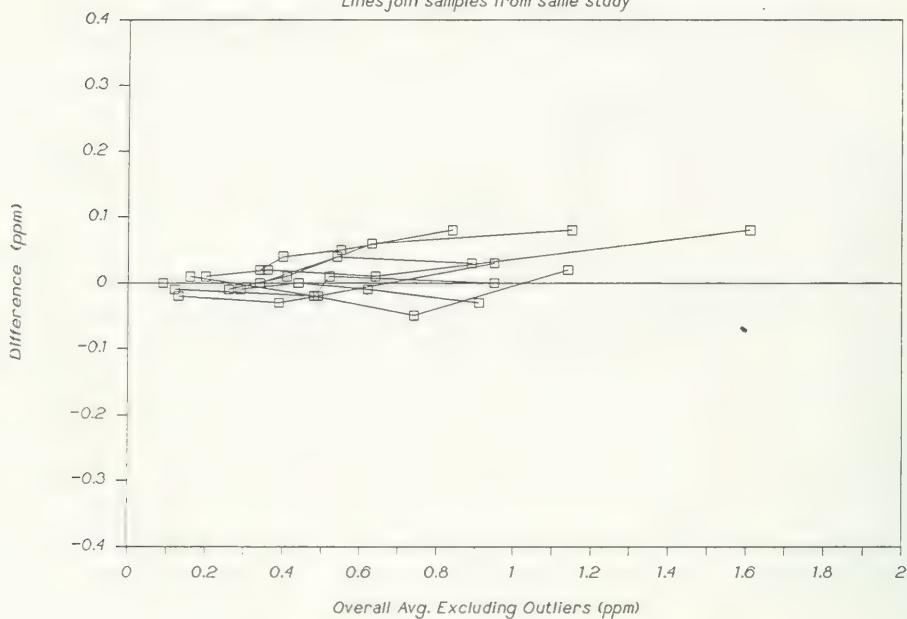


Lab 31



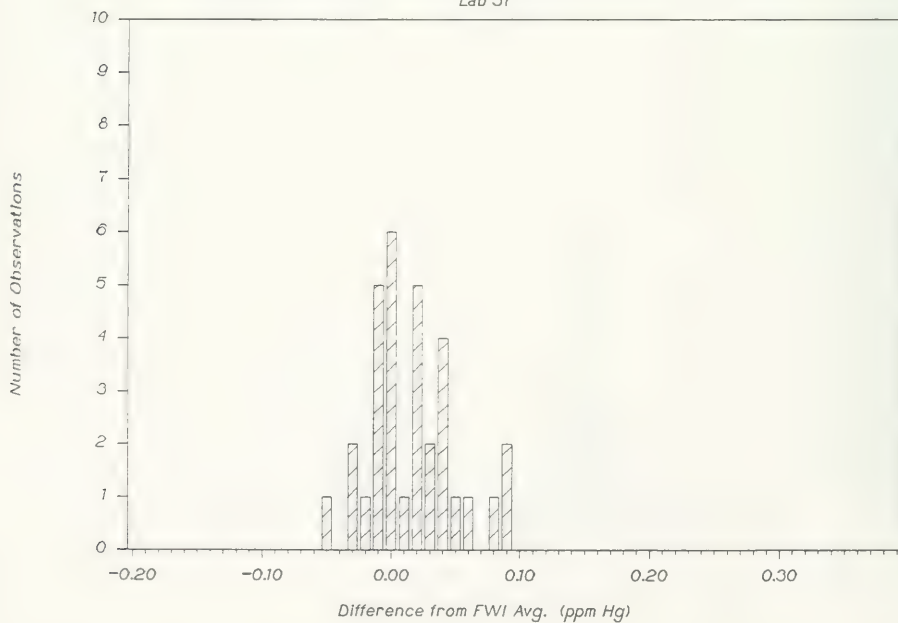
HG IN FISH: LAB 37 DIFFERENCES

Lines join samples from same study



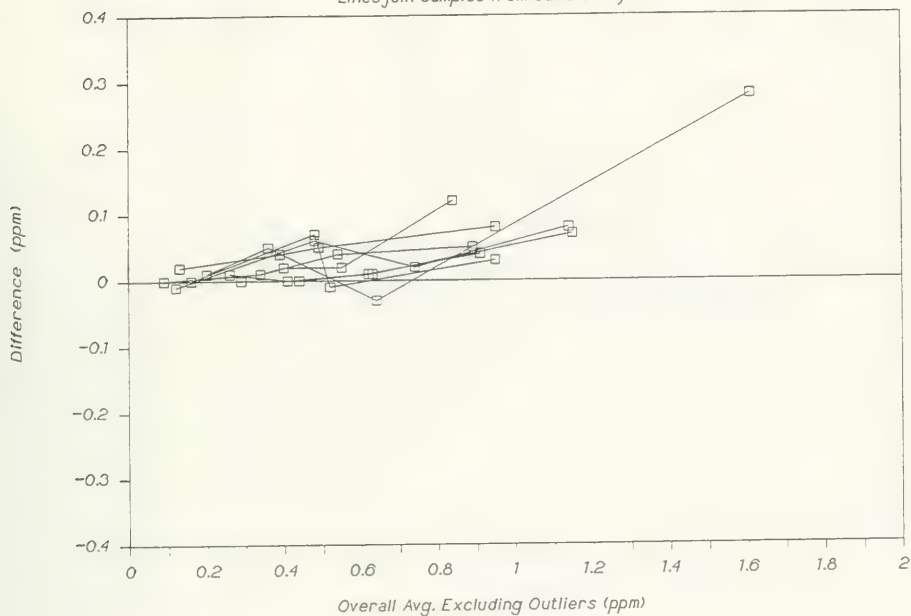
DIFFERENCES FROM FWI AVG.

Lab 37



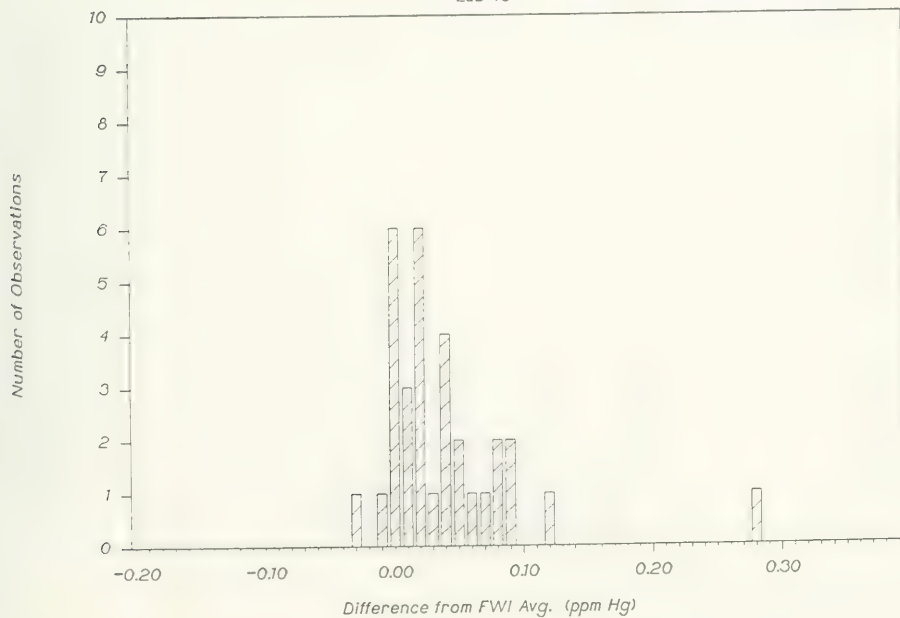
HG IN FISH: LAB 43 DIFFERENCES

Lines join samples from same study

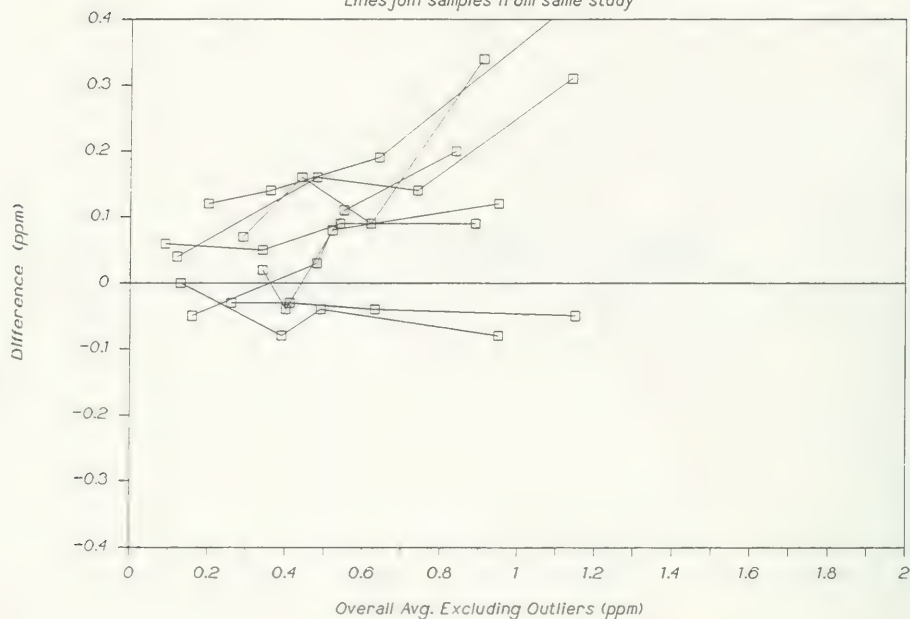


DIFFERENCES FROM FWI AVG.

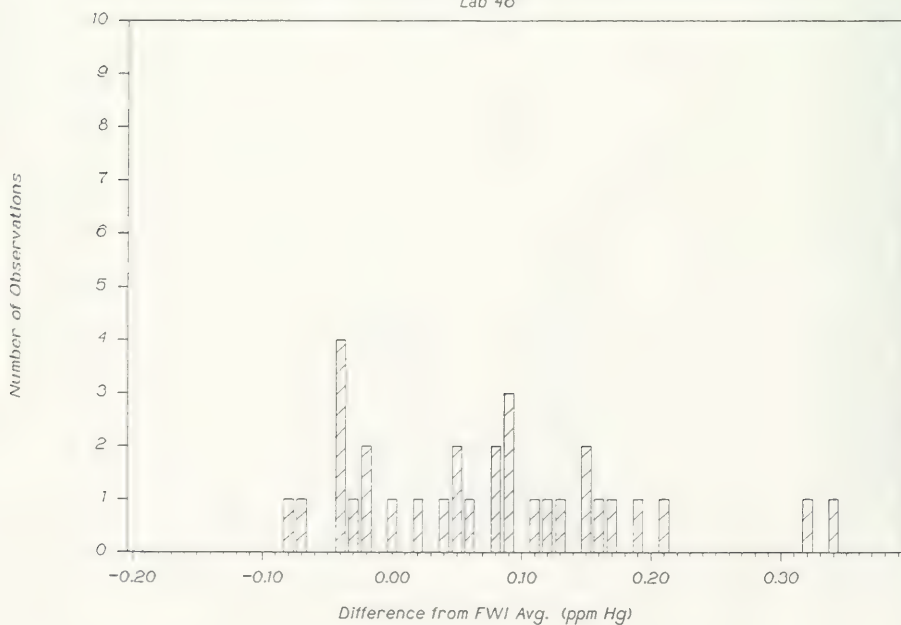
Lab 43



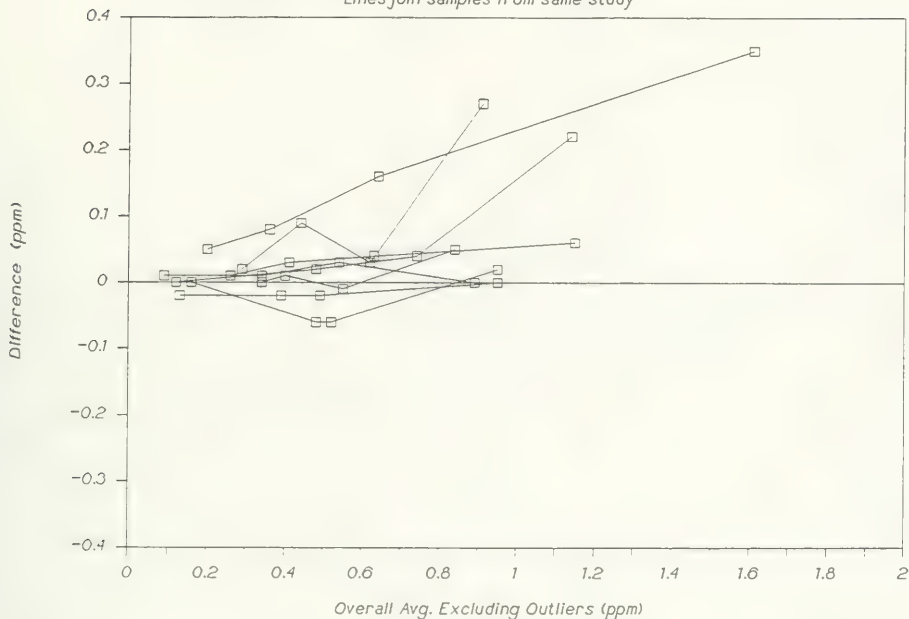
Lines join samples from same study



Lab 46

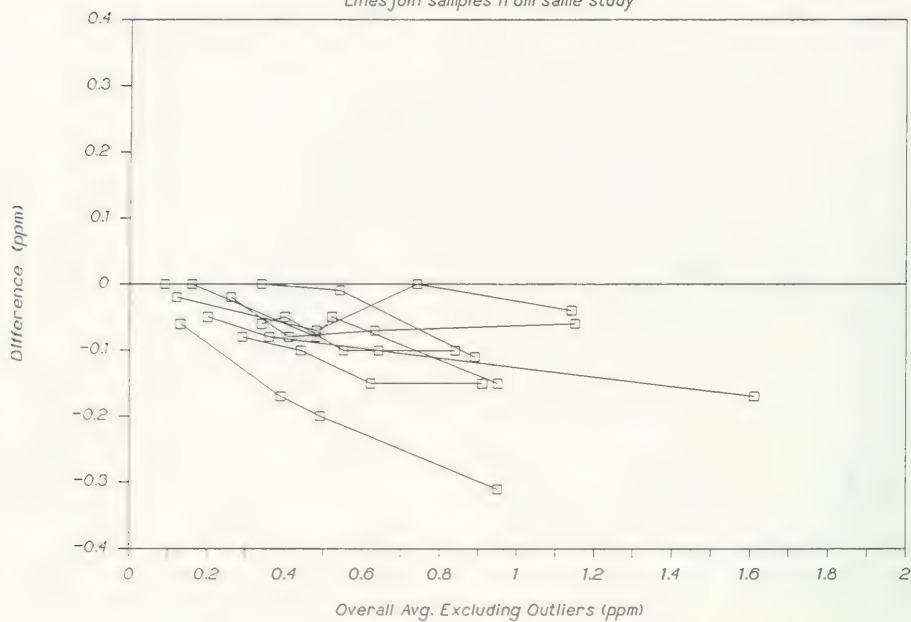


Lines join samples from same study



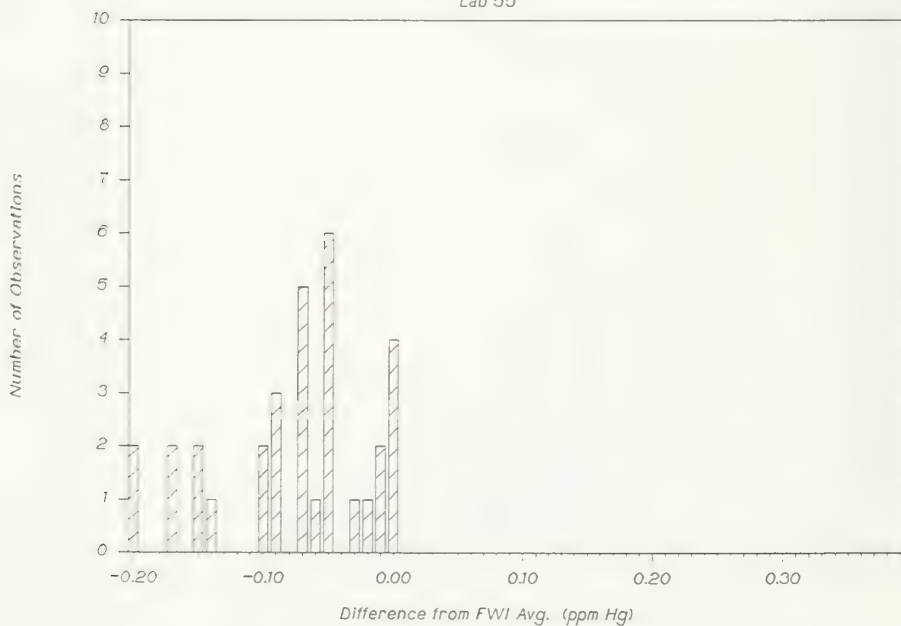
HG IN FISH: LAB 55 DIFFERENCES

Lines join samples from same study



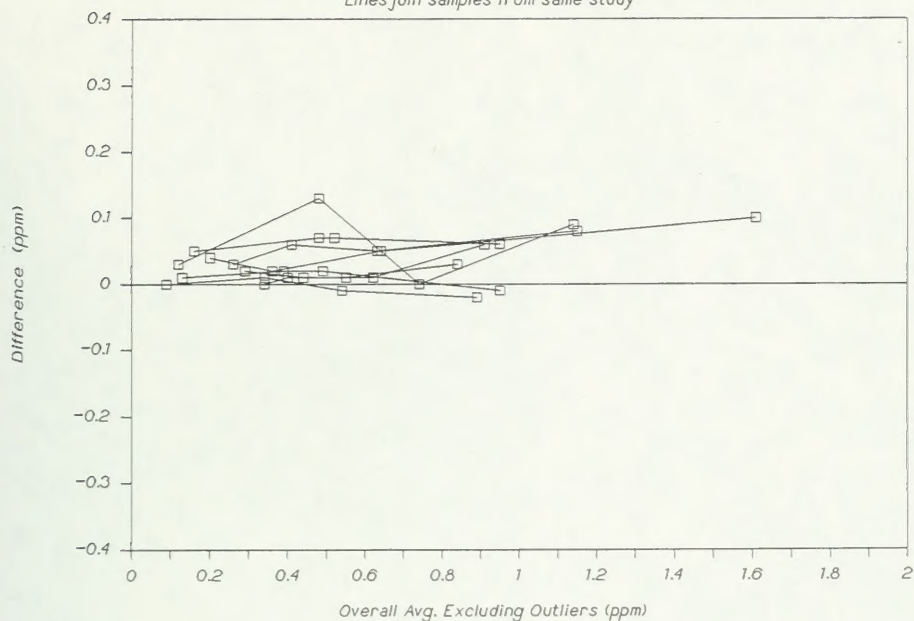
DIFFERENCES FROM FWI AVG.

Lab 55



HG IN FISH: LAB 57 DIFFERENCES

Lines join samples from same study



DIFFERENCES FROM FWI AVG.

Lab 57

